



Distillation Troubleshooting

Henry Z. Kister

Fluor Corporation

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*To my son, Abraham and my wife, Susana, who have been my
love, inspiration, and the lighthouses illuminating my path,
and to my life-long mentor, Dr. Walter Stupin – it is easy to rise
when carried on the shoulders of giants.*

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Contents

Preface xxiii

Acknowledgments xxvii

How to Use this Book xxix

Abbreviations xxxi

1. Troubleshooting Distillation Simulations	1
2. Where Fractionation Goes Wrong	25
3. Energy Savings and Thermal Effects	61
4. Tower Sizing and Material Selection Affect Performance	73
5. Feed Entry Pitfalls in Tray Towers	97
6. Packed-Tower Liquid Distributors: Number 6 on the Top 10 Malfunctions	111
7. Vapor Maldistribution in Trays and Packings	133
8. Tower Base Level and Reboiler Return: Number 2 on the Top 10 Malfunctions	145
9. Chimney Tray Malfunctions: Part of Number 7 on the Top 10 Malfunctions	163
10. Draw-Off Malfunctions (Non-Chimney Tray) Part of Number 7 on the Top 10 Malfunctions	179

11. Tower Assembly Mishaps: Number 5 on the Top 10 Malfunctions	193
12. Difficulties During Start-Up, Shutdown, Commissioning, and Abnormal Operation: Number 4 on the Top 10 Malfunctions	215
13. Water-Induced Pressure Surges: Part of Number 3 on the Top 10 Malfunctions	225
14. Explosions, Fires, and Chemical Releases: Number 10 on the Top 10 Malfunctions	233
15. Undesired Reactions in Towers	237
16. Foaming	241
17. The Tower as a Filter: Part A. Causes of Plugging—Number 1 on the Top 10 Malfunctions	253
18. The Tower as a Filter: Part B. Location of Plugging—Number 1 on the Top 10 Malfunctions	257
19. Coking: Number 1 on the Top 10 Malfunctions	271
20. Leaks	281
21. Relief and Failure	287
22. Tray, Packing, and Tower Damage: Part of Number 3 on the Top 10 Malfunctions	291
23. Reboilers That Did Not Work: Number 9 on the Top 10 Malfunctions	315
24. Condensers That Did Not Work	335
25. Misleading Measurements: Number 8 on the Top 10 Malfunctions	347

26. Control System Assembly Difficulties	357
27. Where Do Temperature and Composition Controls Go Wrong?	373
28. Misbehaved Pressure, Condenser, Reboiler, and Preheater Controls	377
29. Miscellaneous Control Problems	395

DISTILLATION TROUBLESHOOTING DATABASE OF PUBLISHED CASE HISTORIES

1. Troubleshooting Distillation Simulations	398
1.1 VLE	398
1.1.1 Close-Boiling Systems	398
1.1.2 Nonideal Systems	399
1.1.3 Nonideality Predicted in Ideal System	400
1.1.4 Nonideal VLE Extrapolated to Pure Products	400
1.1.5 Nonideal VLE Extrapolated to Different Pressures	401
1.1.6 Incorrect Accounting for Association Gives Wild Predictions	401
1.1.7 Poor Characterization of Petroleum Fractions	402
1.2 Chemistry, Process Sequence	402
1.3 Does Your Distillation Simulation Reflect the Real World?	404
1.3.1 General	404
1.3.2 With Second Liquid Phase	406
1.3.3 Refinery Vacuum Tower Wash Sections	406
1.3.4 Modeling Tower Feed	406
1.3.5 Simulation/Plant Data Mismatch Can Be Due to an Unexpected Internal Leak	406
1.3.6 Simulation/Plant Data Mismatch Can Be Due to Liquid Entrainment in Vapor Draw	407
1.3.7 Bug in Simulation	407
1.4 Graphical Techniques to Troubleshoot Simulations	407
1.4.1 McCabe–Thiele and Hengstebeck Diagrams	407
1.4.2 Multicomponent Composition Profiles	407
1.4.3 Residue Curve Maps	407
1.5 How Good Is Your Efficiency Estimate?	407
1.6 Simulator Hydraulic Predictions: To Trust or Not to Trust	409
1.6.1 Do Your Vapor and Liquid Loadings Correctly Reflect Subcool, Superheat, and Pumparounds?	409
1.6.2 How Good Are the Simulation Hydraulic Prediction Correlations?	409

2. Where Fractionation Goes Wrong 410

- 2.1 Insufficient Reflux or Stages; Pinches 410
- 2.2 No Stripping in Stripper 412
- 2.3 Unique Features of Multicomponent Distillation 412
- 2.4 Accumulation and Hiccups 413
 - 2.4.1 Intermediate Component, No Hiccups 413
 - 2.4.2 Intermediate Component, with Hiccups 414
 - 2.4.3 Lights Accumulation 416
 - 2.4.4 Accumulation between Feed and Top
or Feed and Bottom 417
 - 2.4.5 Accumulation by Recycling 418
 - 2.4.6 Hydrates, Freeze-Ups 418
- 2.5 Two Liquid Phases 419
- 2.6 Azeotropic and Extractive Distillation 421
 - 2.6.1 Problems Unique to Azeotroping 421
 - 2.6.2 Problems Unique to Extractive Distillation 423

3. Energy Savings and Thermal Effects 424

- 3.1 Energy-Saving Designs and Operation 424
 - 3.1.1 Excess Preheat and Precool 424
 - 3.1.2 Side-Reboiler Problems 424
 - 3.1.3 Bypassing a Feed around the Tower 424
 - 3.1.4 Reducing Recycle 425
 - 3.1.5 Heat Integration Imbalances 426
- 3.2 Subcooling: How It Impacts Towers 428
 - 3.2.1 Additional Internal Condensation and Reflux 428
 - 3.2.2 Less Loadings above Feed 429
 - 3.2.3 Trapping Lights and Quenching 429
 - 3.2.4 Others 430
- 3.3 Superheat: How It Impacts Towers 430

4. Tower Sizing and Material Selection Affect Performance 431

- 4.1 Undersizing Trays and Downcomers 431
- 4.2 Oversizing Trays 431
- 4.3 Tray Details Can Bottleneck Towers 433
- 4.4 Low Liquid Loads Can Be Troublesome 434
 - 4.4.1 Loss of Downcomer Seal 434
 - 4.4.2 Tray Dryout 435
- 4.5 Special Bubble-Cap Tray Problems 436
- 4.6 Misting 437
- 4.7 Undersizing Packings 437
- 4.8 Systems Where Packings Perform Different from Expectations 437

4.9	Packed Bed Too Long	438
4.10	Packing Supports Can Bottleneck Towers	439
4.11	Packing Hold-downs Are Sometimes Troublesome	440
4.12	Internals Unique to Packed Towers	440
4.13	Empty (Spray) Sections	440

5. Feed Entry Pitfalls in Tray Towers

441

5.1	Does the Feed Enter the Correct Tray?	441
5.2	Feed Pipes Obstructing Downcomer Entrance	441
5.3	Feed Flash Can Choke Downcomers	441
5.4	Subcooled Feeds, Refluxes Are Not Always Trouble Free	442
5.5	Liquid and Unsuitable Distributors Do Not Work with Flashing Feeds	442
5.6	Flashing Feeds Require More Space	443
5.7	Uneven or Restrictive Liquid Split to Multipass Trays at Feeds and Pass Transitions	443
5.8	Oversized Feed Pipes	444
5.9	Plugged Distributor Holes	444
5.10	Low ΔP Trays Require Decent Distribution	445

6. Packed-Tower Liquid Distributors: Number 6 on the Top 10 Malfunctions

446

6.1	Better Quality Distributors Improve Performance	446
6.1.1	Original Distributor Orifice or Unspecified	446
6.1.2	Original Distributor Weir Type	447
6.1.3	Original Distributor Spray Type	447
6.2	Plugged Distributors Do Not Distribute Well	448
6.2.1	Pan/Trough Orifice Distributors	448
6.2.2	Pipe Orifice Distributors	449
6.2.3	Spray Distributors	450
6.3	Overflow in Gravity Distributors: Death to Distribution	451
6.4	Feed Pipe Entry and Predistributor Problems	454
6.5	Poor Flashing Feed Entry Bottleneck Towers	455
6.6	Oversized Weep Holes Generate Undesirable Distribution	456
6.7	Damaged Distributors Do Not Distribute Well	457
6.7.1	Broken Flanges or Missing Spray Nozzles	457
6.7.2	Others	457
6.8	Hole Pattern and Liquid Heads Determine Irrigation Quality	458
6.9	Gravity Distributors Are Meant to Be Level	459
6.10	Hold-Down Can Interfere with Distribution	460
6.11	Liquid Mixing Is Needed in Large-Diameter Distributors	460
6.12	Notched Distributors Have Unique Problems	461
6.13	Others	461

7. Vapor Maldistribution in Trays and Packings **462**

- 7.1 Vapor Feed/Reboiler Return Maldistributes Vapor to Packing Above 462
 - 7.1.1 Chemical/Gas Plant Packed Towers 462
 - 7.1.2 Packed Refinery Main Fractionators 463
- 7.2 Experiences with Vapor Inlet Distribution Baffles 465
- 7.3 Packing Vapor Maldistribution at Intermediate Feeds and Chimney Trays 465
- 7.4 Vapor Maldistribution Is Detrimental in Tray Towers 466
 - 7.4.1 Vapor Cross-Flow Channeling 466
 - 7.4.2 Multipass Trays 467
 - 7.4.3 Others 467

8. Tower Base Level and Reboiler Return: Number 2 on the Top 10 Malfunctions **468**

- 8.1 Causes of High Base Level 468
 - 8.1.1 Faulty Level Measurement or Level Control 468
 - 8.1.2 Operation 469
 - 8.1.3 Excess Reboiler Pressure Drop 470
 - 8.1.4 Undersized Bottom Draw Nozzle or Bottom Line 470
 - 8.1.5 Others 470
- 8.2 High Base Level Causes Premature Tower Flood (No Tray/Packing Damage) 470
- 8.3 High Base Liquid Level Causes Tray/Packing Damage 471
- 8.4 Impingement by the Reboiler Return Inlet 472
 - 8.4.1 On Liquid Level 472
 - 8.4.2 On Instruments 473
 - 8.4.3 On Tower Wall 473
 - 8.4.4 Opposing Reboiler Return Lines 474
 - 8.4.5 On Trays 474
 - 8.4.6 On Seal Pan Overflow 474
- 8.5 Undersized Bottom Feed Line 475
- 8.6 Low Base Liquid Level 475
- 8.7 Issues with Tower Base Baffles 476
- 8.8 Vortexing 476

9. Chimney Tray Malfunctions: Part of Number 7 on the Top 10 Malfunctions **477**

- 9.1 Leakage 477
- 9.2 Problem with Liquid Removal, Downcomers, or Overflows 478
- 9.3 Thermal Expansion Causing Warping, Out-of-Levelness 479
- 9.4 Chimneys Impeding Liquid Flow to Outlet 480

9.5	Vapor from Chimneys Interfering with Incoming Liquid	480
9.6	Level Measurement Problems	481
9.7	Coking, Fouling, Freezing	482
9.8	Other Chimney Tray Issues	482

10. Drawoff Malfunctions (Non–Chimney Tray): Part of Number 7 on the Top 10 Malfunctions **484**

10.1	Vapor Chokes Liquid Draw Lines	484
10.1.1	Insufficient Degassing	484
10.1.2	Excess Line Pressure Drop	485
10.1.3	Vortexing	486
10.2	Leak at Draw Tray Starves Draw	486
10.3	Draw Pans and Draw Lines Plug Up	488
10.4	Draw Tray Damage Affects Draw Rates	488
10.5	Undersized Side-Stripper Overhead Lines Restrict Draw Rates	488
10.6	Degassed Draw Pan Liquid Initiates Downcomer Backup Flood	489
10.7	Other Problems with Tower Liquid Draws	489
10.8	Liquid Entrainment in Vapor Side Draws	490
10.9	Reflux Drum Malfunctions	490
10.9.1	Reflux Drum Level Problems	490
10.9.2	Undersized or Plugged Product Lines	490
10.9.3	Two Liquid Phases	490

11. Tower Assembly Mishaps: Number 5 on the Top 10 Malfunctions **491**

11.1	Incorrect Tray Assembly	491
11.2	Downcomer Clearance and Inlet Weir Malinstallation	491
11.3	Flow Passage Obstruction and Internals Misorientation at Tray Tower Feeds and Draws	492
11.4	Leaking Trays and Accumulator Trays	493
11.5	Bolts, Nuts, Clamps	493
11.6	Manways/Hatchways Left Unbolted	493
11.7	Materials of Construction Inferior to Those Specified	494
11.8	Debris Left in Tower or Piping	494
11.9	Packing Assembly Mishaps	495
11.9.1	Random	495
11.9.2	Structured	496
11.9.3	Grid	496
11.10	Fabrication and Installation Mishaps in Packing Distributors	496
11.11	Parts Not Fitting through Manholes	498
11.12	Auxiliary Heat Exchanger Fabrication and Assembly Mishaps	498
11.13	Auxiliary Piping Assembly Mishaps	498

12. Difficulties during Start-Up, Shutdown, Commissioning, and Abnormal Operation: Number 4 on the Top 10 Malfunctions **499**

12.1	Blinding/Unblinding Lines	499	
12.2	Backflow	500	
12.3	Dead-Pocket Accumulation and Release of Trapped Materials		501
12.4	Purging	501	
12.5	Pressuring and Depressuring	502	
12.6	Washing	502	
12.7	On-Line Washes	504	
12.8	Steam and Water Operations	506	
12.9	Overheating	506	
12.10	Cooling	507	
12.11	Overchilling	507	
12.12	Water Removal	508	
	12.12.1 Draining at Low Points	508	
	12.12.2 Oil Circulation	508	
	12.12.3 Condensation of Steam Purges	508	
	12.12.4 Dehydration by Other Procedures	508	
12.13	Start-Up and Initial Operation	509	
	12.13.1 Total-Reflux Operation	509	
	12.13.2 Adding Components That Smooth Start-Up	509	
	12.13.3 Siphoning	509	
	12.13.4 Pressure Control at Start-Up	510	
12.14	Confined Space and Manhole Hazards	510	

13. Water-Induced Pressure Surges: Part of Number 3 on the Top 10 Malfunctions **512**

13.1	Water in Feed and Slop	512	
13.2	Accumulated Water in Transfer Line to Tower and in Heater Passes	513	
13.3	Water Accumulation in Dead Pockets	513	
13.4	Water Pockets in Pump or Spare Pump Lines	514	
13.5	Undrained Stripping Steam Lines	515	
13.6	Condensed Steam or Refluxed Water Reaching Hot Section	516	
13.7	Oil Entering Water-Filled Region	517	

14. Explosions, Fires, and Chemical Releases: Number 10 on the Top 10 Malfunctions **518**

14.1	Explosions Due to Decomposition Reactions	518	
	14.1.1 Ethylene Oxide Towers	518	
	14.1.2 Peroxide Towers	519	
	14.1.3 Nitro Compound Towers	520	
	14.1.4 Other Unstable-Chemical Towers	521	

14.2	Explosions Due to Violent Reactions	523
14.3	Explosions and Fires Due to Line Fracture	524
14.3.1	C ₃ –C ₄ Hydrocarbons	524
14.3.2	Overchilling	525
14.3.3	Water Freeze	526
14.3.4	Other	527
14.4	Explosions Due to Trapped Hydrocarbon or Chemical Release	527
14.5	Explosions Induced by Commissioning Operations	528
14.6	Packing Fires	529
14.6.1	Initiated by Hot Work Above Steel Packing	529
14.6.2	Pyrophoric Deposits Played a Major Role, Steel Packing	530
14.6.3	Tower Manholes Opened While Packing Hot, Steel Packing	532
14.6.4	Others, Steel Packing Fires	532
14.6.5	Titanium, Zirconium Packing Fires	533
14.7	Fires Due to Opening Tower before Cooling or Combustible Removal	533
14.8	Fires Caused by Backflow	534
14.9	Fires by Other Causes	535
14.10	Chemical Releases by Backflow	536
14.11	Trapped Chemicals Released	536
14.12	Relief, Venting, Draining, Blowdown to Atmosphere	537

15. Undesired Reactions in Towers

539

15.1	Excessive Bottom Temperature/Pressure	539
15.2	Hot Spots	539
15.3	Concentration or Entry of Reactive Chemical	539
15.4	Chemicals from Commissioning	540
15.5	Catalyst Fines, Rust, Tower Materials Promote Reaction	540
15.6	Long Residence Times	541
15.7	Inhibitor Problems	541
15.8	Air Leaks Promote Tower Reactions	542
15.9	Impurity in Product Causes Reaction Downstream	542

16. Foaming

543

16.1	What Causes or Promotes Foaming?	543
16.1.1	Solids, Corrosion Products	543
16.1.2	Corrosion and Fouling Inhibitors, Additives, and Impurities	544
16.1.3	Hydrocarbon Condensation into Aqueous Solutions	545
16.1.4	Wrong Filter Elements	546
16.1.5	Rapid Pressure Reduction	546
16.1.6	Proximity to Solution Plait Point	546

16.2	What Are Foams Sensitive To?	546
16.2.1	Feedstock	546
16.2.2	Temperature	547
16.2.3	Pressure	547
16.3	Laboratory Tests	547
16.3.1	Sample Shake, Air Bubbling	547
16.3.2	Oldershaw Column	547
16.3.3	Foam Test Apparatus	548
16.3.4	At Plant Conditions	548
16.4	Antifoam Injection	548
16.4.1	Effective Only at the Correct Quantity/Concentration	548
16.4.2	Some Antifoams Are More Effective Than Others	549
16.4.3	Batch Injection Often Works, But Continuous Can Be Better	549
16.4.4	Correct Dispersal Is Important, Too	550
16.4.5	Antifoam Is Sometimes Adsorbed on Carbon Beds	550
16.4.6	Other Successful Antifoam Experiences	550
16.4.7	Sometimes Antifoam Is Less Effective	551
16.5	System Cleanup Mitigates Foaming	551
16.5.1	Improving Filtration	551
16.5.2	Carbon Beds Mitigate Foaming But Can Adsorb Antifoam	553
16.5.3	Removing Hydrocarbons from Aqueous Solvents	553
16.5.4	Changing Absorber Solvent	553
16.5.5	Other Contaminant Removal Techniques	554
16.6	Hardware Changes Can Debottleneck Foaming Towers	555
16.6.1	Larger Downcomers	555
16.6.2	Smaller Downcomer Backup (Lower Pressure Drop, Larger Clearances)	556
16.6.3	More Tray Spacing	556
16.6.4	Removing Top Two Trays Does Not Help	556
16.6.5	Trays Versus Packings	556
16.6.6	Larger Packings, High-Open-Area Distributors Help	557
16.6.7	Increased Agitation	557
16.6.8	Larger Tower	557
16.6.9	Reducing Base Level	557

17. The Tower as a Filter: Part A. Causes of Plugging—Number 1 on the Top 10 Malfunctions

558

17.1	Piping Scale/Corrosion Products	558
17.2	Salting Out/Precipitation	559
17.3	Polymer/Reaction Products	560
17.4	Solids/Entrainment in the Feed	561
17.5	Oil Leak	561

- 17.6 Poor Shutdown Wash/Flush 562
- 17.7 Entrainment or Drying at Low Liquid Rates 562
- 17.8 Others 562

18. The Tower as a Filter: Part B. Locations of Plugging—Number 1 on the Top 10 Malfunctions 563

- 18.1 Trays 563
- 18.2 Downcomers 564
- 18.3 Packings 565
- 18.4 How Packings and Trays Compare on Plugging Resistance 565
 - 18.4.1 Trays versus Trays 565
 - 18.4.2 Trays versus Packings 566
 - 18.4.3 Packings versus Packings 567
- 18.5 Limited Zone Only 567
- 18.6 Draw, Exchanger, and Vent Lines 569
- 18.7 Feed and Inlet Lines 570
- 18.8 Instrument Lines 570

19. Coking: Part of Number 1 on Tower Top 10 Malfunctions 571

- 19.1 Insufficient Wash Flow Rate, Refinery Vacuum Towers 571
- 19.2 Other Causes, Refinery Vacuum Towers 572
- 19.3 Slurry Section, FCC Fractionators 573
- 19.4 Other Refinery Fractionators 574
- 19.5 Nonrefinery Fractionators 574

20. Leaks 575

- 20.1 Pump, Compressor 575
- 20.2 Heat Exchanger 575
 - 20.2.1 Reboiler Tube 575
 - 20.2.2 Condenser Tube 576
 - 20.2.3 Auxiliary Heat Exchanger (Preheater, Pumparound) 576
- 20.3 Chemicals to/from Other Equipment 577
 - 20.3.1 Leaking from Tower 577
 - 20.3.2 Leaking into Tower 577
 - 20.3.3 Product to Product 578
- 20.4 Atmospheric 578
 - 20.4.1 Chemicals to Atmosphere 578
 - 20.4.2 Air into Tower 579

21. Relief and Failure 580

- 21.1 Relief Requirements 580
- 21.2 Controls That Affect Relief Requirements and Frequency 580
- 21.3 Relief Causes Tower Damage, Shifts Deposits 581

21.4	Overpressure Due to Component Entry	581
21.5	Relief Protection Absent or Inadequate	582
21.6	Line Ruptures	583
21.7	All Indication Lost When Instrument Tap Plugged	584
21.8	Trips Not Activating or Incorrectly Set	584
21.9	Pump Failure	585
21.10	Loss of Vacuum	585
21.11	Power Loss	585

22. Tray, Packing, and Tower Damage: Part of Number 3 on the Top 10 Malfunctions **586**

22.1	Vacuum	586
22.2	Insufficient Uplift Resistance	587
22.3	Uplift Due to Poor Tightening during Assembly	587
22.4	Uplift Due to Rapid Upward Gas Surge	589
22.5	Valves Popping Out	590
22.6	Downward Force on Trays	590
22.7	Trays below Feed Bent Up, above Bent Down and Vice Versa	591
22.8	Downcomers Compressed, Bowed, Fallen	592
22.9	Uplift of Cartridge Trays	593
22.10	Flow-Induced Vibrations	593
22.11	Compressor Surge	594
22.12	Packing Carryover	595
22.13	Melting, Breakage of Plastic Packing	595
22.14	Damage to Ceramic Packing	595
22.15	Damage to Other Packings	595

23. Reboilers That Did Not Work: Number 9 on the Top 10 Malfunctions **596**

23.1	Circulating Thermosiphon Reboilers	596
23.1.1	Excess Circulation	596
23.1.2	Insufficient Circulation	596
23.1.3	Insufficient ΔT , Pinching	596
23.1.4	Surging	596
23.1.5	Velocities Too Low in Vertical Thermosiphons	597
23.1.6	Problems Unique to Horizontal Thermosiphons	597
23.2	Once-Through Thermosiphon Reboilers	597
23.2.1	Leaking Draw Tray or Draw Pan	597
23.2.2	No Vaporization/Thermosiphon	598
23.2.3	Slug Flow in Outlet Line	599
23.3	Forced-Circulation Reboilers	599
23.4	Kettle Reboilers	599
23.4.1	Excess ΔP in Circuit	599
23.4.2	Poor Liquid Spread	601
23.4.3	Liquid Level above Overflow Baffle	602

23.5	Internal Reboilers	602	
23.6	Kettle and Thermosiphon Reboilers in Series	603	
23.7	Side Reboilers	603	
	23.7.1 Inability to Start	603	
	23.7.2 Liquid Draw and Vapor Return Problems	603	
	23.7.3 Hydrates	603	
	23.7.4 Pinching	604	
	23.7.5 Control Issues	604	
23.8	All Reboilers, Boiling Side	604	
	23.8.1 Debris/Deposits in Reboiler Lines	604	
	23.8.2 Undersizing	604	
	23.8.3 Film Boiling	604	
23.9	All Reboilers, Condensing Side	605	
	23.9.1 Non condensables in Heating Medium	605	
	23.9.2 Loss of Condensate Seal	605	
	23.9.3 Condensate Draining Problems	606	
	23.9.4 Vapor/Steam Supply Bottleneck	606	
24. Condensers That Did Not Work			607
24.1	Inerts Blanketing	607	
	24.1.1 Inadequate Venting	607	
	24.1.2 Excess Lights in Feed	608	
24.2	Inadequate Condensate Removal	608	
	24.2.1 Undersized Condensate Lines	608	
	24.2.2 Exchanger Design	609	
24.3	Unexpected Condensation Heat Curve	609	
24.4	Problems with Condenser Hardware	610	
24.5	Maldistribution between Parallel Condensers	611	
24.6	Flooding/Entrainment in Partial Condensers	611	
24.7	Interaction with Vacuum and Recompression Equipment	612	
24.8	Others	612	
25. Misleading Measurements: Number 8 on the Top 10 Malfunctions			613
25.1	Incorrect Readings	613	
25.2	Meter or Taps Fouled or Plugged	614	
25.3	Missing Meter	615	
25.4	Incorrect Meter Location	615	
25.5	Problems with Meter and Meter Tubing Installation	616	
	25.5.1 Incorrect Meter Installation	616	
	25.5.2 Instrument Tubing Problems	616	
25.6	Incorrect Meter Calibration, Meter Factor	617	
25.7	Level Instrument Fooled	617	
	25.7.1 By Froth or Foam	617	
	25.7.2 By Oil Accumulation above Aqueous Level	618	
	25.7.3 By Lights	619	

25.7.4	By Radioactivity (Nucleonic Meter)	619
25.7.5	Interface-Level Metering Problems	619
25.8	Meter Readings Ignored	619
25.9	Electric Storm Causes Signal Failure	619

26. Control System Assembly Difficulties 620

26.1	No Material Balance Control	620
26.2	Controlling Two Temperatures/Compositions Simultaneously Produces Interaction	621
26.3	Problems with the Common Control Schemes, No Side Draws	622
26.3.1	Boil-Up on TC/AC, Reflux on FC	622
26.3.2	Boil-Up on FC, Reflux on TC/AC	623
26.3.3	Boil-Up on FC, Reflux on LC	624
26.3.4	Boil-Up on LC, Bottoms on TC/AC	625
26.3.5	Reflux on Base LC, Bottoms on TC/AC	626
26.4	Problems with Side-Draw Controls	626
26.4.1	Small Reflux below Liquid Draw Should Not Be on Level or Difference Control	626
26.4.2	Incomplete Material Balance Control with Liquid Draw	628
26.4.3	Steam Spikes with Liquid Draw	628
26.4.4	Internal Vapor Control makes or Breaks Vapor Draw Control	628
26.4.5	Others	628

27. Where Do Temperature and Composition Controls Go Wrong? 629

27.1	Temperature Control	629
27.1.1	No Good Temperature Control Tray	629
27.1.2	Best Control Tray	630
27.1.3	Fooling by Nonkeys	630
27.1.4	Averaging (Including Double Differential)	631
27.1.5	Azeotropic Distillation	631
27.1.6	Extractive Distillation	631
27.1.7	Other	632
27.2	Pressure-Compensated Temperature Controls	632
27.2.1	ΔT Control	632
27.2.2	Other Pressure Compensation	633
27.3	Analyzer Control	633
27.3.1	Obtaining a Valid Analysis for Control	633
27.3.2	Long Lags and High Off-Line Times	633
27.3.3	Intermittent Analysis	634
27.3.4	Handling Feed Fluctuations	635
27.3.5	Analyzer-Temperature Control Cascade	635
27.3.6	Analyzer On Next Tower	635

28. Misbehaved Pressure, Condenser, Reboiler, and Preheater Controls 636

28.1	Pressure Controls by Vapor Flow Variations	636
28.2	Flooded Condenser Pressure Controls	637
28.2.1	Valve in the Condensate, Unflooded Drum	637
28.2.2	Flooded Drum	637
28.2.3	Hot-Vapor Bypass	637
28.2.4	Valve in the Vapor to the Condenser	639
28.3	Coolant Throttling Pressure Controls	640
28.3.1	Cooling-Water Throttling	640
28.3.2	Manipulating Airflow	640
28.3.3	Steam Generator Overhead Condenser	640
28.3.4	Controlling Cooling-Water Supply Temperature	640
28.4	Pressure Control Signal	641
28.4.1	From Tower or from Reflux Drum?	641
28.4.2	Controlling Pressure via Condensate Temperature	641
28.5	Throttling Steam/Vapor to Reboiler or Preheater	641
28.6	Throttling Condensate from Reboiler	642
28.7	Preheater Controls	643

29. Miscellaneous Control Problems 644

29.1	Interaction with the Process	644
29.2	ΔP Control	644
29.3	Flood Controls and Indicators	644
29.4	Batch Distillation Control	645
29.5	Problems in the Control Engineer's Domain	645
29.6	Advanced Controls Problems	646
29.6.1	Updating Multivariable Controls	646
29.6.2	Advanced Controls Fooled by Bad Measurements	646
29.6.3	Issues with Model Inaccuracies	647
29.6.4	Effect of Power Dips	647
29.6.5	Experiences with Composition Predictors in Multivariable Controls	647

References 649**Index 669****About the Author 713**

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Preface

“To every problem, there’s always an easy solution—neat, plausible, and wrong.”

—Mencken’s Maxim

The last half-century has seen tremendous progress in distillation technology. The introduction of high-speed computers revolutionized the design, control, and operation of distillation towers. Invention and innovation in tower internals enhanced tower capacity and efficiency beyond previously conceived limits. Gamma scans and laser-guided pyrometers have provided troubleshooters with tools of which, not-so-long-ago, they would only dream. With all these advances, one would expect the failure rate in distillation towers to be on the decline, maybe heading towards extinction as we enter the 21st century. Our recent survey of distillation failures (255) brought disappointing news: Distillation failures are not on the path to extinction. Instead, the tower failure rate is on the rise and accelerating.

Our survey further showed that the rise is not because distillation is moving into new, uncharted frontiers. By far, the bulk of the failures have been repetitions of previous ones. In some cases, the literature describes 10–20 repetitions of the same failure. And for every case that is reported, there are tens, maybe hundreds, that are not.

In the late 1980s, I increased tray hole areas in one distillation tower in an attempt to gain capacity. Due to vapor cross flow channeling, a mechanism unknown at the time, the debottleneck went sour and we lost 5% capacity. Half a year of extensive troubleshooting, gamma scans, and tests taught us what went wrong and how to regain the lost capacity. We published extensively on the phenomenon and how to avoid. A decade later, I returned to investigate why another debottleneck (this time by others) went sour at the same unit. The tower I previously struggled with was replaced by a larger one, but the next tower in the sequence (almost the same hydraulics as the first) was debottlenecked . . . by increasing tray hole areas!

It dawned on me how short a memory the process industries have. People move on, the lessons get forgotten, and the same mistakes are repeated. It took only one decade to forget. Indeed, people moved on: only one person (beside me) that experienced the 1980s debottleneck was involved in the 1990s efforts. This person actually questioned

the debottleneck proposal, but was overruled by those who did not believe it will happen again.

Likewise, many experiences are repeatedly reported in the literature. Over the last two decades, there has been about one published case history per year of a tower flooding prematurely due to liquid level rising above the reboiler return nozzle, or of a kettle reboiler bottleneck due to an incorrectly compiled force balance. One would think that had we learned from the first case, all the repetitions could have been avoided. And again, for every case that is reported, there are tens, maybe hundreds that are not.

Why are we failing to learn from past lessons? Mergers and cost-cuts have retired many of the experienced troubleshooters and thinly spread the others. The literature offers little to bridge the experience gap. In the era of information explosion, databases, and computerized searches, finding the appropriate information in due time has become like finding a needle in an evergrowing haystack. To locate a useful reference, one needs to click away a huge volume of wayward leads. Further, cost-cutting measures led to library closures and to curtailed circulation and availability of some prime sources of information, such as, AIChE meeting papers.

The purpose of this book is pick the needles out of the haystack. The book collects lessons from past experiences and puts them in the hands of troubleshooters in a usable form. The book is made up of two parts: the first is a collection of “war stories,” with the detailed problems and solutions. The second part is a database mega-table which presents summaries of all the “war stories” I managed to find in the literature. The summaries include some key distillation-related morals. For each of these, the literature reference is described fully, so readers can seek more details. Many of the case histories could be described under more than one heading, so extensive cross references have been included.

If an incident that happened in your plant is described, you may notice that some details could have changed. Sometimes, this was done to make it more difficult for people to tell where the incident occurred. At other times, this was done to simplify the story without affecting the key lessons. Sometimes, the incident was written up several years after it occurred, and memories of some details faded away. Sometimes, and this is the most likely reason, the case history did not happen in your plant at all. Another plant had a similar incident.

The case histories and lessons drawn are described to the best of my and the contributors' knowledge and in good faith, but do not always correctly reflect the problems and solutions. Many times I thought I knew the answer, possibly even solved the problem, only to be humbled by new light or another experience later. The experiences and lessons in the book are not meant to be followed blindly. They are meant to be taken as stories told in good faith, and to the best of knowledge and understanding of the author or contributor. We welcome any comments that either affirm or challenge our perception and understanding.

If you picked the book, you expressed interest in learning from past experiences. This learning is an essential major step along the path traveled by a good troubleshooter or designer. Should you select this path, be prepared for many sleepless nights in the plant, endless worries as to whether you have the right answer, tests that will

shatter your favorite theories, and many humbling experiences. Yet, you will share the glory when your fix or design solves a problem where others failed. You will enjoy harnessing the forces of nature into a beneficial purpose. Last but not least, you will experience the electric excitement of the “moments of insight,” when all the facts you have been struggling with for months suddenly fall together into a simple explanation. I hope this book helps to get you there.

HENRY Z. KISTER

March 2006

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Acknowledgments

Many of the case histories reported in this book have been invaluable contributions from colleagues and friends who kindly and enthusiastically supported this book. Many of the contributors elected to remain anonymous. Kind thanks are due to all contributors. Special thanks are due to those who contributed multiple case histories, and to those whose names do not appear in print. To those behind-the-scenes friends, I extends special appreciation and gratitude.

Writing this book required breaking away from some of the everyday work demands. Special thanks are due to Fluor Corporation, particularly to my supervisors, Walter Stupin and Paul Walker, for their backing, support and encouragement of this book-writing effort, going to great lengths to make it happen.

Recognition is due to my mentors who, over the years, encouraged my work, immensely contributed to my achievements, and taught me much about distillation and engineering: To my life-long mentor, Walter Stupin, who mentored and encouraged my work, throughout my career at C F Braun and later at Fluor, being a ceaseless source of inspiration behind my books and technical achievements; Paul Walker, Fluor, whose warm encouragement and support have been the perfect motivators for professional excellence and achievement; Professor Ian Doig, University of NSW, who inspired me over the years, showed me the practical side of distillation, and guided me over a crisis early in my career; Reno Zack, who enthusiastically encouraged and inspired my achievements throughout my career at C F Braun; Dick Harris and Trevor Whalley, who taught me about practical distillation and encouraged my work and professional pursuits at ICI Australia; and Jack Hull, Tak Yanagi, and Jim Gosnell, who were sources of teaching and inspiration at C F Braun. The list could go on, and I express special thanks to all that encouraged, inspired, and contributed to my work over the years. Much of my mentors' teachings found their way into the following pages.

Special thanks are due to family members and close friends who have helped, supported and encouraged my work—my mother, Dr. Helen Kister, my father, Dr. John Kister, and Isabel Wu—your help and inspiration illuminated my path over the years.

Last but not least, special thanks are due to Mireille Grey and Stan Okimoto at Fluor, who flawlessly and tirelessly converted my handwritten scrawl into a typed manuscript, putting up with my endless changes and reformat.

H.Z.K.

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How to Use this Book

The use of this book as a story book or bedtime reading is quite straight forward and needs no guidance. Simply select the short stories of specific interest and read them.

More challenging is the use of this book to look for experiences that could have relevance to a given troubleshooting endeavor. Here the database mega-Table in the second part of the book is the key. Find the appropriate subject matter via the table of contents or index, and then explore the various summaries, including those in the cross-references. The database mega-Table also lists any case histories that are described in full in this book. Such case histories will be prefixed “DT” (acronym for Distillation Troubleshooting). For instance, if the mega-Table lists DT2.4, it means that the full experience is reported as case history 2.4 in this book.

The database as well as many of the case histories list only some of the key lessons drawn. The lessons listed are not comprehensive, and omit nondistillation morals (such as the needs for more staffing or better training). The reader is encouraged to review the original reference for additional valuable lessons.

For quick reference, the acronyms used in Distillation Troubleshooting are listed up front, and the literature references are listed alphabetically.

Some of the case histories use English units, others use metric units. The units used often reflect the unit system used in doing the work. The conversions are straightforward and can readily be performed by using the conversion tables in Perry’s Handbook (393) or other handbooks.

The author will be pleased to hear any comments, experiences or challenges any readers may wish to share for possible inclusion in a future edition. Also, the author is sure that despite his intensive literature search, he missed several invaluable references, and would be very grateful to receive copies of such references. Feedback on any errors, as well as rebuttal to any of the experiences described, is also greatly appreciated and will help improve future editions. Please write, fax or e-mail to Henry Z. Kister, Fluor, 3 Polaris Way, Aliso Viejo, CA 92698, phone 1-949-349-4679; fax 1-949-349-2898; e-mail *henry.kister@fluor.com*.

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Abbreviations

AC	Analyzer control
AGO	Atmospheric gas oil
aMDEA	Activated MDEA
AMS	Alpha-methyl styrene
APC	adaptive process control
AR	on-line analyzer
ASTM	American Society for Testing and Materials
atm	atmospheres, atmospheric
B	Bottoms
barg	bars, gauge
BFW	Boiler feed water
BMD	2-bromomethyl-1, 3-dioxolane
BPD	Barrels per day
BPH	Barrels per hour
BSD	bottom side draw
BTEX	Benzene, toluene, ethylbenzene, xylene
BTX	Benzene, toluene, xylene
C ₁ , C ₂ , C ₃ ...	Number of carbon atoms in compound
CAT	computed axial tomography
Cat	Catalytic
C-factor	Vapor capacity factor, defined by equation 2 in Case Study 1.14
CFD	computational fluid dynamics
CHP	cumene hydroperoxide
CO ₂	Carbon dioxide
Co.	Company
CS	Carbon steel
CT	Chimney Tray
CTC	Carbon tetrachloride
CW	Cooling water
CWR	Cooling water return
CWS	Cooling water supply
D	Distillate
D86	ASTM atmospheric distillation test of petroleum fraction

xxxii Abbreviations

DAA	diacetone alcohol
DC ₁	Demethanizer
DC ₂	Deethanizer
DC ₃	Depropanizer
DC ₄	Debutanizer
DC ₅	Depentanizer
DCM	Dichloromethane
DCS	Distributed control system
DEA	Diethanol amine
DFNB	2, 4-difluoronitrobenzene
DIB	Deisobutanizer
DMAC	dimethylacetamide
DMC	Dynamic matrix control
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
DO	Decant oil
<i>dP</i>	Same as ΔP
DQI	Distribution quality index
DRD	distillation region diagram
<i>dT</i>	Same as ΔT
DT	Distillation troubleshooting (this book)
EB	Energy balance; ethylbenzene
ED	extractive distillation
EDC	Ethylene dichloride
EG	Ethylene glycol
EGEE	Ethylene glycol monoethyl ether
EO	ethylene oxide
EOR	End of run
ETFE	Ethylene tetrafluoroethylene, a type of teflon
FC	Flow control
FCC	Fluid catalytic cracker
FI	Flow indicator
fph	feet per hour
FR	Flow recorder
FS	Flow Switch
ft	Feet
gal	gallons
GC	Gas chromatographs
GC-MS	Gas chromatography–mass spectrometry
gpm	gallons per minute
GS	A process of concentrating deuterium by dual-temperature isotope exchange between water and hydrogen sulfide with no catalyst
h	hours
H ₂	Hydrogen
H ₂ O	Water

H ₂ S	Hydrogen sulfide
HA	Hydroxyl amine
HAZOP	Hazard and operability study
HC	Hydrocarbon
HCGO	Heavy coker gas oil
HCl	Hydrogen chloride
HCN	Hydrogen cyanide
HCO	Heavy cycle oil
HD	Heavy diesel
HETP	Height equivalent of a theoretical plate
HF	Hydrogen fluoride
Hg	Mercury
HK	Heavy key
HN	Heavy naphtha
HP	High pressure
HR	High reflux
HSS	Heat-stable salts
HV	hand valve
HVGO	Heavy vacuum gas oil
IBP	Initial boiling point
ICO	intermediate cycle oil
ID	Internal diameter
IK	Intermediate key
in.	inch
IPA	Isopropyl alcohol
IPE	Isopropyl ether
IR	Infrared
IVC	Internal vapor control
kPa	Kilopascals
kPag	Kilopascals gage
lb	pounds
LC	Level control
LCGO	Light coker gas oil
LCO	Light cycle oil
LD	Light diesel
LI	Level indicator
LK	Light key
LL	Liquid-liquid
LMTD	Log mean temperature difference
LP	Low pressure
LPB	Loss Prevention Bulletin
LPG	Liquefied petroleum gas; refers to C ₃ and C ₄ hydrocarbons
LR	Low reflux
LT	Level transmitter
L/V	Liquid-to-vapor molar ratio

xxxiv Abbreviations

LVGO	Light vacuum gas oil
m	meters
MB	Material balance
MDEA	Methyl diethanol amine
MEA	Monoethanol amine
MEK	Methyl ethyl ketone
MF	Main fractionator
min	Minutes or minimum
MISO	Multiple inputs, single output
mm	millimeters
MNT	Mononitrotoluene
MOC	Management of change
MP	Medium Pressure
MPC	Model predictive control
mpy	mils per year, refers to a measure of conosion rates. 1 mil is 1/1000 inch
MSDS	Material safety data sheets
MTS	Refers to a proprietary liquid distributor marketed by Sulzer under license from Dow Chemical
MV	Manual valve
MVC	Multivariable control, or more volitle component
N ₂	nitrogen
NC	Normally closed
NGL	Natural gas liquids
NNF	Normally no flow
NO	Normally open
NPSH	Net positive suction head
NRTL	Nonrandom two liquid; refers to a popular VLE prediction method
NRU	Nitrogen rejection unit
O ₂	oxygen
ORS	Oxide redistillation still
OSHA	Occupational Safety and Health Administration
PA	Pumparound
P&ID	Process and instrumentation diagram
PC	Pressure control
PCV	Pressure control valve
PI	Pressure indicator
PR	Peng–Robinson; refers to a popular VLE prediction method
psi	pounds per square inch
psia	psi absolute
psig	psi gauge
PSV	Pressure safety valve
PT	Pressure transmitter
PVC	Polyvinyl chloride
PVDF	Polyvynilidene fluoride
R22	Freon 22

R/D	Reflux-to-distillate molar ratio
Ref.	Reference
Refrig	Refrigeration
RO	Restriction orifice
RVP	Reid vapor pressure
s	seconds
SBE	Di- <i>Sec</i> -butyl ether
sec.	secondary
SG	specific gravity
SPA	Slurry pumparound
SRK	Soave, Redlich, and Kwong; refers to a popular VLE method
SS	Stainless steel
STM	Steam
T/A	Turnaround
TBP	True boiling point
TC	Temperature control
TCE	Trichloroethylene
TDC	Temperature difference controller
TEA	Triethanol amine
TEG	Triethylene glycol
TI	Temperature indicator
Ti	Titanium
TRC	temperature recorder/controller
UNIQAC	Unified quasi-chemical; refers to a popular VLE prediction method
VAM	Vinyl acetate monomer
V/B	Stripping ratio, i.e., molar ratio of stripping section vapor flow rate to tower bottom flow rate
VCFC	Vapor cross-flow channeling
VCM	Vinyl chloride monomer
VGO	Vacuum gas oil
VLE	Vapor–liquid equilibrium
VLLE	Vapor–liquid–liquid equilibrium
VOC	Volatile organic carbon
vol	Volume
w.g.	water gage
wt	by weight
ΔP	Pressure difference
ΔT	Temperature difference

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Chapter 1

Troubleshooting Distillation Simulations

It may appear inappropriate to start a distillation troubleshooting book with a malfunction that did not even make it to the top 10 distillation malfunctions of the last half century. Simulations were in the 12th spot (255). Countering this argument is that simulation malfunctions were identified as the fastest growing area of distillation malfunctions, with the number reported in the last decade about triple that of the four preceding decades (252). If one compiled a distillation malfunction list over the last decade only, simulation issues would have been in the equal 6th spot. Simulations have been more troublesome in chemical than in refinery towers, probably due to the difficulty in simulating chemical nonidealities. The subject was discussed in detail in another paper (247).

The three major issues that affect simulation validity are using good vapor–liquid equilibrium (VLE) predictions, obtaining a good match between the simulation and plant data, and applying graphical techniques to troubleshoot the simulation (255). Case histories involving these issues account for about two-thirds of the cases reported in the literature. Add to this ensuring correct chemistry and correct tray efficiency, these items account for 85% of the cases reported in the literature.

A review of the VLE case studies (247) revealed major issues with VLE predictions for close-boiling components, either a pair of chemicals [e.g., hydrocarbons (HCs)] of similar vapor pressures or a nonideal pair close to an azeotrope. Correctly estimating nonidealities has been another VLE troublespot. A third troublespot is characterization of heavy components in crude oil distillation, which impacts simulation of refinery vacuum towers. Very few case histories were reported with other systems. VLE prediction for reasonably ideal, relatively high volatility systems (e.g., ethane–propane or methanol–ethanol) is not frequently troublesome.

The major problem in simulation validation appears to be obtaining a reliable, consistent set of plant data. Getting correct numbers out of flowmeters and laboratory analyses appears to be a major headache requiring extensive checks and rechecks. Compiling mass, component, and energy balances is essential for catching a

misleading flowmeter or composition. One specific area of frequent mismatches between simulation and plant data is where there are two liquid phases. Here comparison of measured to simulated temperature profiles is invaluable for finding the second liquid phase. Another specific area of frequent mismatches is refinery vacuum towers. Here the difficult measurement is the liquid entrainment from the flash zone into the wash bed, which is often established by a component balance on metals or asphaltenes.

The key graphical techniques for troubleshooting simulations are the McCabe–Thiele and Hengstebeck diagrams, multicomponent distillation composition profiles, and in azeotropic systems residue curve maps. These techniques permit visualization and insight into what the simulation is doing. These diagrams are not drawn from scratch; they are plots of the composition profiles obtained by the simulation using the format of one of these procedures. The book by Stichlmair and Fair (472) is loaded with excellent examples of graphical techniques shedding light on tower operation.

In chemical towers, reactions such as decomposition, polymerization, and hydrolysis are often unaccounted for by a simulation. Also, the chemistry of a process is not always well understood. One of the best tools for getting a good simulation in these situations is to run the chemicals through a miniplant, as recommended by Ruffert (417).

In established processes, such as separation of benzene from toluene or ethanol from water, estimating efficiency is quite trouble free in conventional trays and packings. Problems are experienced in a first-of-a-kind process or when a new mass transfer device is introduced and is on the steep segment of its learning curve.

Incorrect representation of the feed entry is troublesome if the first product leaves just above or below or if some chemicals react in the vapor and not in the liquid. A typical example is feed to a refinery vacuum tower, where the first major product exits the tower between 0.5 and 2 stages above the feed.

The presentation of liquid and vapor rates in the simulation output is not always user friendly, especially near the entry of subcooled reflux and feeds, often concealing higher vapor and liquid loads. This sometimes precipitates underestimates of the vapor and liquid loads in the tower.

Misleading hydraulic predictions from simulators is a major trouble spot. Most troublesome have been hydraulic predictions for packed towers, which tend to be optimistic, using both the simulator methods and many of the vendor methods in the simulator (247, 254). Simulation predictions of both tray and packing efficiencies as well as downcomer capacities have also been troublesome. Further discussion is in Ref. 247.

CASE STUDY 1.1 METHANOL IN C₃ SPLITTER OVERHEAD?

Installation Olefins plant C₃ splitter, separating propylene overhead from propane at pressures of 220–240 psig, several towers.

Background Methanol is often present in the C₃ splitter feed in small concentrations, usually originating from dosing upstream equipment to remove hydrates. Hydrates are loose compounds of water and HCs that behave like ice, and methanol is used like antifreeze. The atmospheric boiling points of propylene, propane, and methanol are -54 , -44 , and 148°F , respectively. The C₃ splitters are large towers, usually containing between 100 and 300 trays and operating at high reflux, so they have lots of separation capability.

Problem Despite the large boiling point difference (about 200°F) and the large tower separation capability, some methanol found its way to the overhead product in all these towers. Very often there was a tight specification on methanol in the tower overhead.

Cause Methanol is a polar component, which is repelled by the nonpolar HCs. This repulsion is characterized by a high activity coefficient. With the small concentration of methanol in the all-HC tray liquid, the repulsion is maximized; that is, the activity coefficient of methanol reaches its maximum (infinite dilution) value. This high activity coefficient highly increases its volatility, to the point that it almost counterbalances the much higher vapor pressure of propylene. The methanol and propylene therefore become very difficult to separate.

Simulation All C₃ splitter simulations that the author worked with have used equations of state, and these were unable to correctly predict the high activity coefficient of the methanol. They therefore incorrectly predicted that all the methanol would end up in the bottom and none would reach the tower top product.

Solution In most cases, the methanol was injected upstream for a short period only, and the off-specification propylene product was tolerated, often blended in storage. In one case, the methanol content of the propylene was lowered by allowing some propylene out of the C₃ splitter bottom at the expense of lower recovery.

Related Experience A very similar experience occurred in a gas plant depropanizer separating propane from butane and heavier HCs. Here the methanol ended in the propane product.

Other Related Experiences Several refinery debutanizers that separated C₃ and C₄ [liquefied petroleum gases (LPGs)] from C₅ and heavier HCs (naphtha) contained small concentrations of high-boiling sulfur compounds. Despite their high boiling points (well within the naphtha range), these high boilers ended in the overhead LPG product. Sulfur compounds are polar and are therefore repelled by the HC tray liquid. The repulsion (characterized by their infinite dilution activity coefficient) made these compounds volatile enough to go up with the LPG. Again, tower simulations that were based on equations of state incorrectly predicted that these compounds would end up in the naphtha.

In one refinery and one petrochemical debutanizer, mercury compounds with boiling points in the gasoline range were found in the LPG, probably reaching it by a similar mechanism.

CASE STUDY 1.2 WATER IN DEBUTANIZER: QUO VADIS?

Installation A debutanizer separating C_4 HCs from HCs in the C_5 – C_8 range. Feed to the tower was partially vaporized in an upstream feed-bottom interchanger. The feed contained a small amount of water. Water has a low solubility in the HCs and distilled up. The reflux drum was equipped with a boot designed to gravity-separate water from the reflux.

Problem When the feed contained a higher concentration of water or the reflux boot was inadvertently overfilled, water was seen in the tower bottoms.

Cause The tower feed often contained caustic. Caustic deposits were found in the tower at shutdown. Sampling the water in the tower bottom showed a high pH. Analysis showed that the water in the bottom was actually concentrated caustic solution.

Prevention Good coalescing of water and closely watching the interface level in the reflux drum boot kept water out of the feed and reflux. Maximizing feed preheat kept water in the vapor.

CASE STUDY 1.3 BEWARE OF HIGH HYDROCARBON VOLATILITIES IN WASTEWATER SYSTEMS

Benzene was present in small concentration, of the order of ppm, in a refinery wastewater sewer system. Due to the high repulsion between the water and benzene molecules, benzene has a high activity coefficient, making it very volatile in the wastewater.

Poor ventilation, typical of sewer systems, did not allow the benzene to disperse, and it concentrated in the vapor space above the wastewater. The lower explosive limit of benzene in air is quite low, about a few percent, and it is believed that the benzene concentration exceeded it at least in some locations in the sewer system.

The sewer system had one vent pipe discharging at ground level without a goose-neck. A worker was doing hot work near the top of that pipe. Sparks are believed to have fallen into the pipe, igniting the explosive mixture. The pipe blew up into the worker's face, killing him.

Morals

- Beware of high volatilities of HCs and organics in a wastewater system.
- Avoid venting sewer systems at ground level.

CASE STUDY 1.4 A HYDROCARBON VLLE METHOD USED FOR AQUEOUS FEED EQUILIBRIUM

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Installation Feed for a methanol–water separation tower was the water–methanol phase from a three-phase gas–oil–aqueous separator. Gas from the separator was moderately high in H_2S and in CO_2 . Tower preliminary design used a total overhead condenser to produce 95% methanol. Methanol product was cooled and stored at atmospheric pressure. Off gas from storage was not considered a problem because the calculated impurities in the methanol product were predominantly water.

Problem Tower feed had been calculated with a standard gas-processing vapor–liquid–liquid equilibrium (VLLE) method (Peng–Robinson equation of state). A consultant noted that the VLLE method applied only to aqueous phases that behaved like pure water and only to gas-phase components that had low solubility in the aqueous phase.

The large methanol content of the aqueous phase invalidated these feed composition calculations. Every gas component was far more soluble in the tower feed than estimated. The preliminary tower design would have produced a methanol product with such a high H_2S vapor pressure that it could not be safely stored in the atmospheric tank.

Better Approach Gas solubility in a mixed, non-HC solvent (methanol and water) is a Henry's constant type of relationship for which process simulation packages often do not have the methods and/or parameters required.

Addition of a pasteurization section to the top of a tower is a common fix for removing light impurities from the distillate product. After condensing most of the overhead vapor, a small overhead vent gas stream is purged out of the tower to remove light ends. Most or all of the overhead liquid is refluxed to minimize loss of desired product in the purges. The pasteurization section typically contains 3–10 trays or a short packed bed, used to separate light ends from the distillate product. The distillate product is taken as a liquid side draw below the pasteurization trays. The side draw may be stripped to further reduce light ends. The vent gas may be refrigerated and solvent washed or otherwise treated to reduce loss of desired product.

Solution An accurate, specific correlation (outside of the process simulation package) was used to calculate H_2S and CO_2 concentration in the methanol–water tower feed. Solubility of HC components was roughly estimated because they were at relatively low concentrations in the tower feed. A high-performance coalescer was used to minimize liquid HC droplets in the tower feed.

A pasteurization section was added to the top of the tower. The overhead vent gas purge stream was designed to remove most of the H_2S , CO_2 , and light HCs. Downstream recovery of methanol from the vent gas and stripping of the methanol product side draw were considered but found to be uneconomical.

Moral Poor simulation and design result from poor selection of VLE and VLLE methods. Computer output does not include a warning when the selected VLE method produces garbage.

CASE STUDY 1.5 MODELING TERNARY MIXTURE USING BINARY INTERACTION PARAMETERS

Contributed by Stanislaw K. Wasylikiewicz, Aspen Technology, Inc., Calgary, Alberta, Canada

This case study describes a frequently encountered modeling problem during simulation of heterogeneous azeotropic distillation. Phase diagrams are invaluable for troubleshooting this type of simulation problems.

Distillation Simulation A sequence of distillation columns for separation of a mixture containing water and several organic alcohols was set up in a simulator. Since some of the alcohols are not fully miscible with water, a nonrandom two-liquid (NRTL) model was selected to model VLLE in the system. At atmospheric pressure, the vapor phase was treated as an ideal gas.

Problem Simulation of the sequence of distillation columns never converged, giving many warnings about flash failures.

Investigation For the three key components (methanol, water, and *n*-butanol) a phase diagram was created (508) (Fig. 1.1*a*). As expected, the water–methanol and methanol–*n*-butanol edges are homogeneous and the water–*n*-butanol edge contained an immiscibility gap. Surprisingly, the three-liquid region and three two-liquid regions covered almost the entire composition space. Since water and methanol, as well as butanol and methanol, are fully miscible, the diagram should have been dominated by a single-liquid region. Just looking at the phase diagram one can conclude that the model is not correct.

Analysis Binary interaction parameters for activity models used for VLLE calculations are published for thousands of components [see, e.g., DECHEMA (158) series]. They are regressed based on various experimental data and usually fit the experimental points quite well. NRTL, UNIQUAC, and Wilson models extend these binary data to multicomponent systems without requiring additional ternary, quaternary, and so on, interaction parameters. That is why these models are so popular for modeling VLE for strongly nonideal azeotropic mixtures. This extension, however, is not always performed correctly by the model.

For the ternary mixture methanol–water–*n*-butanol, the binary interaction parameters have been taken from DECHEMA (158). Some of them are recommended values. All of them describe all the binary pairs very well. But what they predict when combined together can be seen in Figure 1.1*a*. Notice that to create this VLLE diagram an extremely robust flash calculation with stability test is essential. Without a reliable global stability test, flash calculation can easily fail at some points in this component space or give unstable solutions (526).

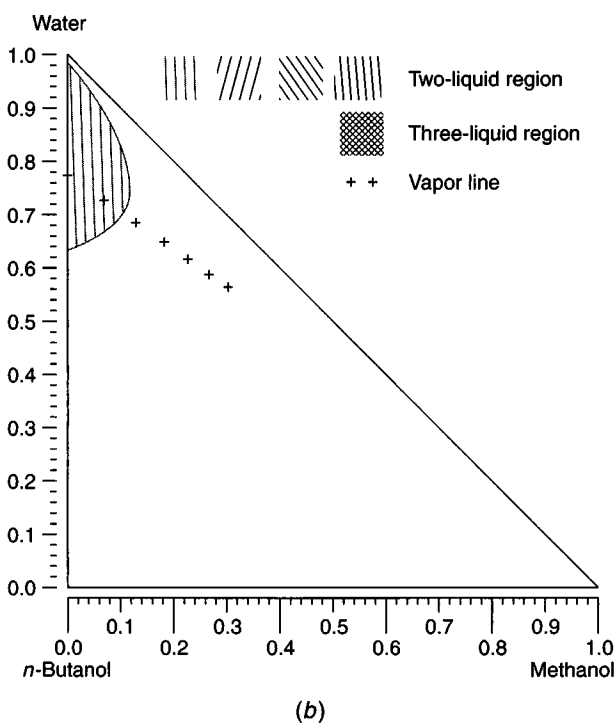
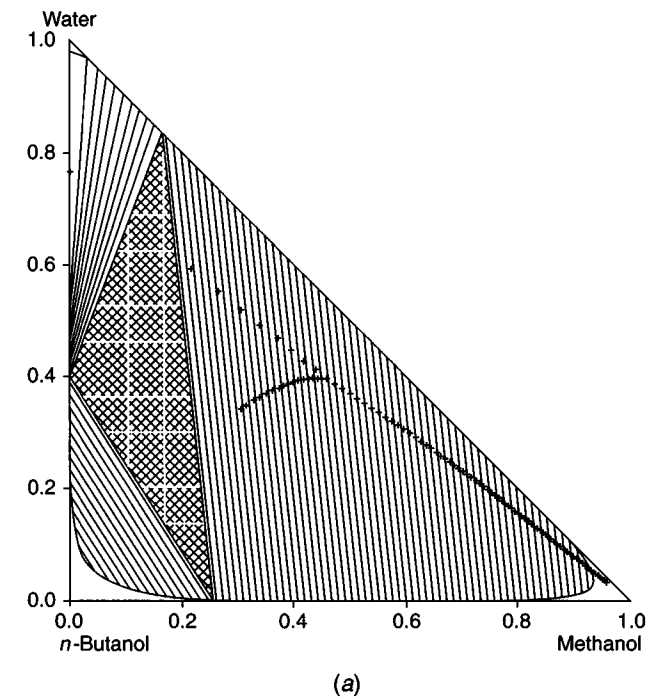


Figure 1.1 Phase diagram for nonideal system methanol–water–*n*-butanol, based on extension of good binary data using NRTL model: (a) incorrect extension; (b) correct extension.

Solution Another set of binary interaction parameters was carefully selected and a new phase diagram was recreated (34). The VLLE changed dramatically (Fig. 1.1*b*). There is no more three-liquid phase region and only one two-liquid phase region covers only a small part of the composition space. After proper selection of interaction parameters of the thermodynamic model, the sequence of distillation columns converged quickly without any problems.

Morals

- To simulate multicomponent, nonideal distillation, the behavior of the mixture must be carefully verified, starting from binary mixtures, then ternary subsystems, and so on.
- Since there may be many pairs of binary interaction parameters of an activity thermodynamic model that describe behavior of a binary mixture equally well, it is recommended to select one with the lowest absolute values. It is our experience that such values extrapolate better to multicomponent mixtures.
- To correctly create a multicomponent, nonideal VLLE model, an extremely robust VLLE calculation routine with a reliable global stability test is a must [even if liquid–liquid (LL) split is not expected].
- Because of their visualization capabilities, VLLE phase diagrams are invaluable (for ternary and quaternary mixtures) for verification of thermodynamic models used in distillation simulations.

CASE STUDY 1.6 VERY LOW CONCENTRATIONS REQUIRE EXTRA CARE IN VLE SELECTION

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Problem Bottoms from a tower recovering methanol from a methanol–water mixture contained 6 ppm methanol, exceeding the maximum specification of 4 ppm required for discharging to the ocean.

Investigation A consultant pointed out that unusual hydrogen-bonding behavior had been reported at very low concentration of methanol in water. He recommended use of the UNIQUAC equation.

Wilson's equation is generally the method of choice for alcohol–water mixtures when there is no unusual behavior. The more complex NRTL equation is the usual choice for systems that cannot be handled by Wilson's equation. The UNIQUAC equation often applies to systems with chemically like interactions (i.e., hydrogen bonding, which behaves like weak chemical bonding) that neither Wilson's nor the NRTL equations can represent.

Solution Schedule constraints precluded independently developing UNIQUAC parameters. Various process simulation packages were checked for methanol–water VLE with Wilson's, NRTL, and UNIQUAC equations. All of the equations in all of the packages gave essentially the same VLE, except that UNIQUAC in one major

simulator gave lower methanol relative volatilities (by as much as 15%) at very low methanol concentrations. This package executed much slower than the other alternatives. The only methanol concentration predictions that were in line with the field data came from this UNIQUAC equation.

Postmortem Exceptions to the typical choices of chemical VLE methods are often not reflected in process simulation packages. For this case, the same data base was probably used by all of the process simulation packages for the regression of UNIQUAC parameters. Predicting VLE for high-purity mixture often requires extrapolation of activity coefficients. Only one method and one simulation package did a good extrapolation to the low-methanol end. Cross checking of VLE equations and packages is a useful way to identify potential problems.

CASE STUDY 1.7 DIAGRAMS TROUBLESHOOT ACETIC ACID DEHYDRATION SIMULATION

Contributed by Stanislaw K. Wasylikiewicz, Aspen Technology, Inc., Calgary, Alberta, Canada

This case study describes a typical thermodynamic modeling problem in distillation simulation and an application of residue curve maps for troubleshooting and proper model selection. The problem described here happened far too many times for many of our clients.

Dehydration of Acetic Acid At atmospheric pressure, there is no azeotrope in the binary mixture of water and acetic acid. However, there is a tangent pinch close to pure water. This makes this binary separation very expensive if only a small concentration of acetic acid in water is allowed (high reflux, many rectifying stages). The difficult separation caused by the tangent pinch can be avoided by adding an entrainer that forms a new heterogeneous azeotrope, moving the distillation profile away from the binary pinch toward the minimum-boiling heterogeneous azeotrope. A decanter can then be used to obtain required distillate purity in far fewer stages than in the original binary distillation (525).

Distillation Simulation A column with top decanter was set up in a simulator to remove water from a mixture containing mostly water and acetic acid. *N*-Butyl acetate was selected as an entrainer. The vapor phase was treated as an ideal gas [*Idel* (227) option]. For the liquid phase, the NRTL model was selected.

Problem Even with an extreme reflux and a large number of stages, the simulation never achieved the required high-purity water in the bottom product of the column.

Troubleshooting For the three key components (water, acetic acid, and the entrainer) a distillation region diagram (DRD) was created (227) to examine the three-component space for multiple liquid regions, azeotropes, and distillation boundaries, as shown in Figure 1.2a.

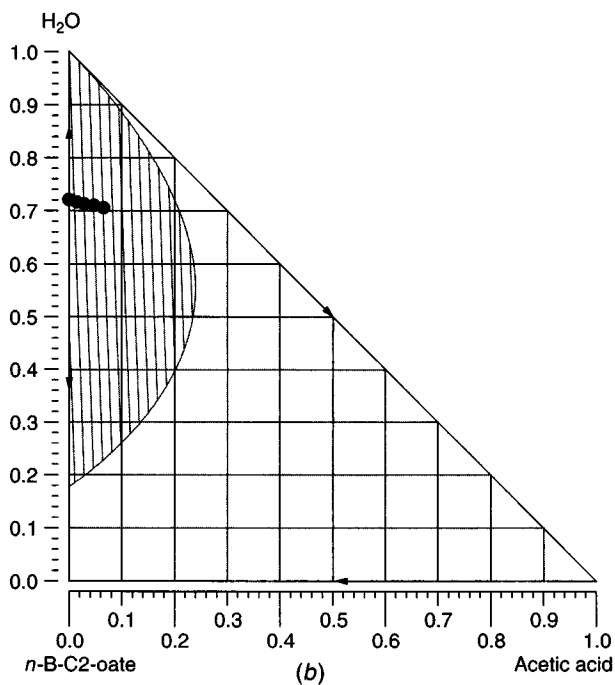
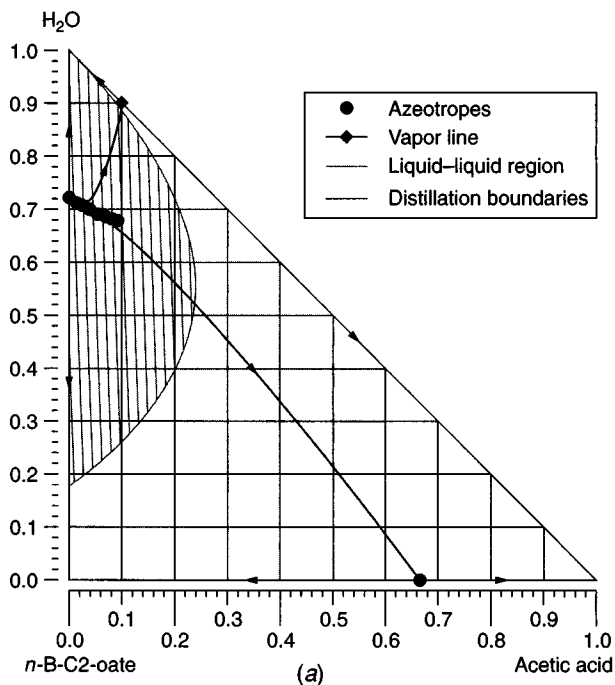


Figure 1.2 Phase diagram for dehydration of acetic acid using n -butyl acetate ($n\text{-B-C2-oate}$) entrainer at 1 atm: (a) with ideal vapor phase, incorrect; (b) accounting for dimerization, correct.

Analysis By examining the DRD, one can easily conclude that there is something wrong with the model. We know that there is no binary acetic acid–water azeotrope at 1 atm. The model (ideal vapor phase) is not capable of describing the system properly. It is well known that carboxylic acids associate in the vapor phase and this has to be taken into account, for example, by vapor dimerization model (158) [*Dimer* option (227)].

Solution Instead of *Idel*, the *Dimer* option was selected (227). The DRD for the system changed tremendously (see Fig. 1.2*b*). There are no more binary azeotropes between acetic acid and water or *n*-butyl acetate. After proper selection of the thermodynamic model, the distillation column converged quickly to the required high-purity water specifications in the bottoms.

Morals

- It is important to select the proper thermodynamic model and carefully verify the behavior of the mixture.
- Because of their visualization capabilities, DRDs are extremely useful for evaluating thermodynamic models for ternary and quaternary mixtures.

CASE STUDY 1.8 EVERYTHING VAPORIZED IN A CRUDE VACUUM TOWER SIMULATION

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Problem Atmospheric crude tower bottom was heated, then entered a typical, fuel-type vacuum tower. A hand-drawn curve estimated the atmospheric crude tower bottom composition from assay distillation data for a light crude oil. The simulation estimated that all of the vacuum tower feed vaporized in the flash zone. This was a preposterous result inconsistent with plant data.

Investigation The heaviest assay cuts fell progressively lower than those from another assay of the same crude oil. The heaviest cut was at 850°F atmospheric cut point, compared to the other assay at 1000°F. The assay data were extrapolated on a linear scale to 100% at 1150°F atmospheric boiling point.

The high-boiling part of crude assay data must be carefully assessed. The last several assay points are often poor, particularly when coming from laboratories that cut back on quality control for increased productivity. Crude oils have very high boiling point material. Even light crude oils have material boiling above 1500°F. Extrapolation should be done with percent distilled on a probability-type scale, particularly for light crudes where the slope increases very rapidly on a linear scale.

Solution A new boiling point curve was developed. Another assay was used up to 1000°F cut point, thus reducing the needed extrapolation range. Extrapolation and smoothing of assay data were based upon a probability scale for percent distilled.

A 95% point (whole crude oil basis) of 1400°F was estimated by this extrapolation. Simulation based upon the new boiling point curve was in reasonable agreement with plant data.

Moral Crude oil high-boiling-point data are often poor and must be extrapolated. Experience, following good procedures, and cross checks with plant data are essential for reliable results.

CASE STUDY 1.9 CRUDE VACUUM TOWER SIMULATION UNDERESTIMATES RESIDUE YIELD

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

Problem Process simulation estimated much lower vacuum residue yields than obtained from plant towers and from pilot unit runs. Vacuum tower feed boiling point curves were based upon high-temperature gas chromatography (GC) analyses.

Investigation Vacuum tower feed boiling point curves from the GC fell well below curves estimated from assays. The GC analyses assumed that all of the feed oil vaporized in the test and was analyzed.

The highest boiling part of crude oil is too heavy to vaporize in a GC test. Thus the reported GC results did not include the highest boiling part (that above about 1250°F boiling point) of the feed. Simulations based upon this GC data estimated much higher vaporization than actual because they were missing the heaviest part of the feed.

Solution The GC method was modified to include a standard that allowed estimation of how much oil remained in the GC column and was not measured. New GC data and extrapolations of assay data indicated that 10–15% of the feed oil was not vaporized and thus had not been measured by the earlier GC method.

With this improved GC data, simulations agreed well with most of the pilot data. The agreement between simulation and plant data was much better than before but was still not good. This may have been due to poor plant data. Specifically, measured flash zone pressures were often bad.

Moral The analyses used for process simulations must be thoroughly understood.

CASE STUDY 1.10 MISLED BY ANALYSIS

Contributed by Geert Hangx and Marleen Horsels, DSM Research, Geleen, The Netherlands

Problem After a product change in a multipurpose plant, a light-boiling by-product could not be removed to the proper level in the (batch) distillation. The concentration

of the light-boiling component in the final product was 0.5%. It should have been (and was in previous runs) 200 ppm.

Investigation The feed was analyzed by GC per normal procedure. The concentration levels of different components looked good. No significant deviation was found. Then some changes in the distillation were performed, such as

- increasing the “lights fraction” in the batch distillation,
- increasing the reflux ratio during the lights fraction, and
- decreasing the vapor load during the lights fraction.

These changes yielded no significant improvement.

The off-specification product was redistilled. The purity was improved, but still the specification could not be met. The GC analysis was checked (recalibrated) again. Everything was OK.

As all of the above-mentioned actions did not improve the product quality, it seemed that something was wrong with the column. After long discussions it was decided to open the handhole at the top of the column and to have a closer look at the feed distributor. Nothing suspicious was found.

Then it was decided to have a closer look at the analysis again. A gas chromatography–mass spectrometry (GC-MS) analysis was performed. This method showed that the impurity was not the light-boiling component as presumed. This component was a remainder from the previous run in the multipurpose plant. Having a boiling point much closer to the end product, this component could not be separated in the column.

Moral It is a good idea to check the analysis with GC-MS before shutting down a column.

CASE STUDY 1.11 INCORRECT FEED CHARACTERIZATION LEADS TO IMPOSSIBLE PRODUCT SPECIFICATIONS

Contributed by Chris Wallsgrove

Installation A new, entirely conventional depentanizer, recovering a C₅ distillate stream from a C₅/C₆/C₇ raffinate mixture from a catalytic reformer/aromatics extraction unit, with some light pyrolysis gasoline feed from an adjacent naphtha-cracking ethylene plant. The column had 30 valve trays, a steam-heated reboiler, and a condenser on cooling water.

Problem The C₅ distillate was guaranteed by the process licensor to contain a maximum of 0.5% wt. C₆'s. Laboratory testing by the on-site laboratory as well

as an impartial third-party laboratory consistently showed about 1.0% of C_6 's in the distillate. Increasing reflux ratio or other operation adjustments did not improve distillate purity.

Troubleshooting The tower was shut down after about 6 weeks of operation to inspect the trays. No damage was found and the trays were reported to be “cleaner than new.”

The design simulation was rerun with a variety of options: correlations, convergence criteria, and plant analysis data. The laboratory methods, which were established American Society for Testing and Materials (ASTM) test methods, were reviewed. It became apparent that the feed contained some low-boiling components, such as certain methyl-cyclo C_5 's which were analyzed (correctly) as C_6 's but whose boiling points are in the C_5 range. Since these components would end up in the distillate, it was thermodynamically impossible to achieve the specified performance.

Solution The higher impurity level could be lived with without excessive economic penalty and was accepted.

Moral Correct characterization of feed components is essential even for an “ideal” hydrocarbon mixture.

CASE STUDY 1.12 CAN YOU NAME THE KEY COMPONENTS?

**Henry Z. Kister, reference 254. Reproduced with permission.
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Installation A stabilizer separating C_3 and lighter HCs from nC_4 and heavier operated at its capacity limit. It was to be debottlenecked for a 25% increase in capacity. In addition, it was required to handle several different feedstocks at high throughputs. Due to the tight requirements, thorough tests were conducted and formed the basis for a simulation, which was used for the debottlenecking. We have seen very few tests as extensive and thorough as the stabilizer tests. Two tests were conducted: a high-reflux (HR) test and a low-reflux (LR) test.

Simulation Versus Measurement With two seemingly minor and insignificant exceptions, all reliable measurements compared extremely well with simulated values. In most tests, the accuracy and reliability of the data would have made it difficult to judge whether the exceptions were real or reflected a minor test data problem. In this case, however, consistency checks verified that the exceptions were real. The high accuracy and reliability of the test data made even small discrepancies visible and significant.

The discrepancies occurred in the HR test, while the LR test showed no discrepancy. This was strange because the stabilizer was extremely steady and smooth during the HR test. Any data problems should have occurred in the LR test or in both tests, but not in the HR test alone.

The two exceptions were interlinked. For the HR test, the simulation predicted three times the measured C_5 concentration in the stabilizer overhead, which would lead to a warmer rectifying section. Indeed, the second exception was simulated rectifying section temperatures 2–5°F warmer than measured.

What Does the Stabilizer Do? At first glance, this question appears stupid. But it turned out to be the key for understanding the test versus the simulation discrepancy.

There was a tight specification on the content of C_3 in the stabilizer bottoms. An excessive amount of C_3 would lead to excessive Reid vapor pressure (RVP) in the bottom, which was undesirable. For similar reasons, it was desirable to minimize iC_4 in the stabilizer bottom, although there was *no* set specification. In the bottoms, nC_4 and heavier were desirable components and were to be maximized. Any C_5 and heavier, and even nC_4 , ending up in the overhead product incurred an economic penalty because the bottoms were far more valuable than the overheads. There were no set specifications for any of these components.

With the above in mind, what is the stabilizer actually doing? Which pair is the key components? Initially, we thought it was iC_4/nC_4 —but could it have been C_3/iC_4 , nC_4/C_5 , C_3/C_5 , or maybe some other pair? Computer simulations do not answer such questions; Hengstebeck diagrams (211, described in detail in Ref. 251) do.

Hengstebeck diagrams (Fig. 1.3) were prepared from the compositions calculated by the simulation. The HR and LR tests each require one Hengstebeck diagram for each choice of key components: C_3/iC_4 , iC_4/nC_4 , and nC_4/iC_5 . A Hengstebeck diagram for the iC_4/nC_4 separation was included in a more detailed description of the case (254) and showed that this pair behaved the same as the C_3/iC_4 pair.

Figure 1.3a shows that in the HR test, below the feed, the stabilizer effectively separated C_3 and lighter from iC_4 and heavier. The diagram also shows that a limited degree of separation of these components occurred in the top two stages of the rectifying section, but pinching occurred below these. Overall, very little separation of C_3 and lighter from iC_4 and heavier occurred in the rectifying section. The stabilizer essentially behaved as a stripper for separating C_3 and lighter from iC_4 and heavier.

Figure 1.3b shows that in the HR test, above the feed, the stabilizer effectively separated nC_4 and lighter from iC_5 and heavier. It also illustrates that some separation of these components took place in the bottom five stages of the stripping section, but pinching occurred above these.

Together, Figures 1.3a and b underscore that the stripping section of the stabilizer separated C_3 and lighter from iC_4 and heavier and, per Ref. 254, also iC_4 and lighter from nC_4 and heavier. The rectifying section of the stabilizer separated iC_5 and heavier from nC_4 and lighter.

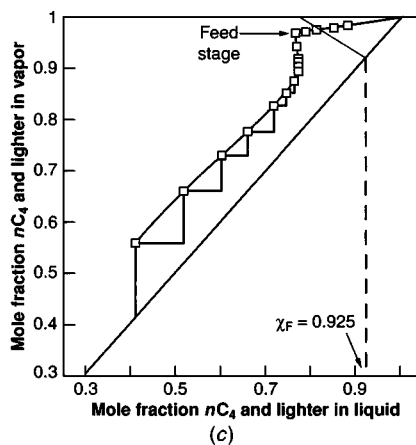
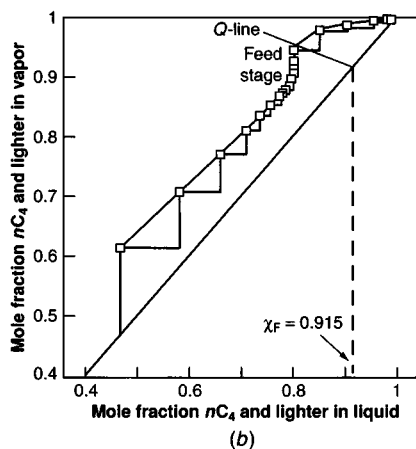
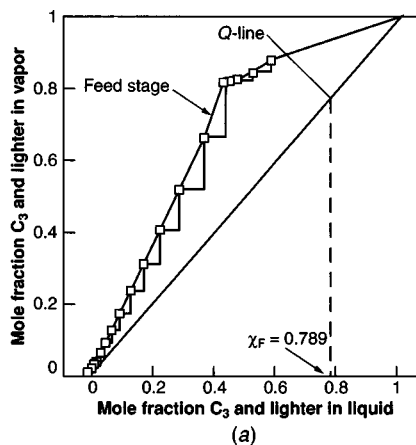


Figure 1.3 Hengstebeck diagrams for stabilizer tests: (a) C_3 - iC_4 separation, HR test; (b) nC_4 - iC_5 separation, HR test; (c) nC_4 - iC_5 separation, LR test. (From Ref. 254. Reproduced with permission. Copyright © (1995) AIChE. All rights reserved.)

In the LR test, the Hengstebeck diagrams for the C_3/iC_4 and iC_4/nC_4 separation were similar to those for the HR test (Fig. 1.3a). In this test, too, the stabilizer stripping section effectively separated C_3 and lighter from iC_4 and heavier and iC_4 and lighter from nC_4 and heavier.

Figure 1.3c indicates that in the LR test, above the feed, the separation of nC_4 and lighter from iC_5 and heavier was pinched. This is different from the HR test, where the rectifying section effectively separated nC_4 and lighter from iC_5 and heavier. The diagram also shows that, as in the HR test, the nC_4/iC_5 separation was pinched in the stripping section.

Overall, the stabilizer behavior in the LR test resembled that of HR test, with the exception that the rectifying section, which separated nC_4 from iC_5 in the HR test, was pinched and did little of this separation in the LR test.

Why the Differences Between Measurement and Simulation? There were two conceivable explanations to the high C_5 concentration in the HR test simulation:

1. *Inaccuracies in VLE data.* Detailed checks of the VLE confirmed that the values used were very good and superior to those predicted by the commercial simulator program, but not perfect. Two relevant inaccuracies were a high C_3/iC_4 volatility prediction for the stripping section and a low C_4/C_5 volatility prediction for the rectifying section.
2. *Efficiency differences between different binary pairs.* This explanation was unlikely because the simulation would suggest a considerably higher efficiency for the higher volatility pair, nC_4/iC_5 , than for the lower volatility pair, iC_4/nC_4 . In contrast, test data (52, 379, 381) show that lower volatility pairs have a higher efficiency.

It was therefore concluded that VLE inaccuracy is the most likely explanation.

One unanswered question is why the differences between measurement and simulation were observed only in the HR test and not in the LR test. Again, the Hengstebeck diagrams provided the answer.

For the HR test, the Hengstebeck diagram (Fig. 1.3b) shows that the rectifying section rectifies C_5 from the nC_4 and lighter. Any error in the relative volatility of the nC_4/iC_5 and nC_4/nC_5 pairs is magnified at each separation stage. The final result is a large difference between measured and simulated top-product compositions.

For the LR test, the Hengstebeck diagram (Fig. 1.3c) shows very little separation of nC_4 from C_5 in the rectifying section. Because of the pinch, an error in the relative volatility of the nC_4/iC_5 and nC_4/nC_5 pairs is not magnified in each separation stage. Such an error, therefore, has little effect on the separation and the temperature profile. For this reason, the LR test simulation gave a good match to measured data.

Would the Inaccuracy Affect the Debottlenecking Predictions? The simulation predicted higher C_5 in the top product, giving a conservative forecast of

the stabilizer performance under test conditions. The remaining question is whether the simulation will continue to give conservative predictions under different process conditions. The question of extrapolating test data into different process conditions is addressed rigorously on pp. 400–405 of Ref. 251. In fact, the analysis in Ref. 251 was part of the stabilizer-debottlenecking assignment. The conclusion reached was that when test data are simulated with too low a volatility the simulation compensates by using a greater number of stages (and, hence, higher efficiencies) to match the measured separation. In this case (e.g., the nC_4/C_5 pair in the stabilizer), the simulation will continue to give conservative predictions when extrapolated into different process conditions.

The converse occurs when test data are simulated with too high a relative volatility. The simulation compensates by using a smaller number of stages to match the measured separation. In this case (e.g., the C_3/iC_4 pair in the stabilizer), extrapolation to other process conditions will be optimistic, sometimes grossly so.

Based on the above, it was concluded that the simulation was a reliable basis for debottlenecking for the base case (similar feedstock to that used in one of the tests) and for alternative feedstocks that are not widely different from the base case. However, for those cases of feedstock variations where feed composition varied widely from the base case, the simulation could not be used with confidence until the inaccuracy in the C_3/iC_4 relative volatility was mitigated.

Postmortem The column was successfully debottlenecked. The same simulation (modified to account for the debottlenecking hardware modifications) was found to give superb predictions of the post-revamp performance.

CASE STUDY 1.13 LOCAL EQUILIBRIUM FOR CONDENSERS IN SERIES

Contributed by W. Randall Hollowell, CITGO, Lake Charles, Louisiana

This is my all-time favorite fractionation simulation problem. The entire refinery capacity was sometimes limited by the gas rate, which was calculated to be zero.

Installation An atmospheric crude distillation tower had an extremely broad boiling range overhead vapor with significant ethane, high propane, through full-range kerosene. There were three long, double split-flow condensers in series. The shells were flange to flange and located directly above the overhead accumulator.

Problem Simulation predicted a zero off-gas rate at peak summer temperatures. But actual off-gas rates were substantial, even in winter. Summer crude charge rate was sometimes reduced to avoid flaring of gas in excess of compressor capacity. There was a strong economic incentive to increase butane spiking of crude, but this was not done due to concerns that the gas rate would increase.

Component Balances Earlier calculations had failed to obtain an adequate material balance of the lightest components in the overhead. The naphtha GC analyses were found to be poor. Procedures were corrected by the laboratory, and good material balance closures were obtained.

Simulations predicted that all of the exiting vapor off gas should have been absorbed into the naphtha stream at the operating temperature and pressure. The naphtha had much lower light-ends concentrations than predicted: 30% of the predicted for propane, 50% for butanes, and 75% for pentanes concentration. These low concentrations in the naphtha provided the vapor off-gas flow.

With many sets of data, each giving good material balance closure, it was obvious that the vapor exiting the overhead accumulator was not in equilibrium with liquid exiting the accumulator. Condensers fouled severely on the tube side, but this did not explain the large deviations from equilibrium.

Theory Conventional process simulation assumes what can be called the “universal VLE model.” This model assumes that VLE is universal, that is, holds at every location, between the total vapor flow and the total liquid flow. In shell-side condensation, the liquid and vapor are usually close to equilibrium locally when the liquid condenses on the tube surface. But after the liquid drops off the tube (and to the bottom of the shell), there is not enough vapor–liquid mixing to maintain equilibrium with the downstream vapor. Thus there is usually “local VLE” at the tube surface, but not universal VLE for the system. This local equilibrium is responsible for the phenomena of subcooled refluxes coexisting with uncondensed vapor. Condensers designed for total condensation have frequently been partial condensers because of local VLE.

Deviations from universal equilibrium can be large for condensers in series with broad boiling range mixtures. Deviations are particularly high for mixtures with high light-ends content and for arrangements where the liquid stays largely separated from the downstream vapor. This case study represents an extreme example of these deviations.

For the overhead accumulator, universal VLE requires that the operating pressure and the exiting liquid bubble point pressure be equal. But bubble point pressure was half of the operating pressure. If the entire exiting vapor flow had been absorbed into the naphtha stream, the bubble point pressure would still have been less than the operating pressure.

Solution A model was developed to more closely represent the condensation steps. Liquid condensed in each shell was assumed to be in equilibrium with the gas leaving that shell. After the liquid left the shell in which it condensed, it was assumed to have zero mass transfer with the gas phase but to be cooled to the local operating temperature. This model had only one-third of the total liquid (the one-third that condensed in the last shell) in equilibrium with the off gas. The other two-thirds of the liquid was much heavier and caused the overall liquid bubble point pressure to be about half that of the liquid that condensed in the last shell. The actual system was

more complex than the above model, in particular:

- The liquid condensed in each shell was heavier than the calculated liquid in equilibrium with the exiting vapor.
- Liquid condensed in an upstream shell experienced a moderate amount of mixing (and thus mass transfer) with downstream vapor.

The above two effects are in opposite directions and largely cancel each other for this case study (perhaps because of the double-split arrangement and three shells in series). This cancellation of errors caused the model to adequately match actual liquid composition and actual vapor rate leaving the overhead accumulator.

Morals For broad boiling range mixtures, condensers (particularly condensers in series) have less capacity than estimated by conventional simulation with universal VLE. This is a failure in simulation and design rather than an equipment failure.

A simulation based upon good operating data can often be used to adequately model the effect of local equilibrium. Good heat and material balances and confidence in them are necessary to step away from universal VLE assumptions and obtain realistic simulations.

Process designers have compensated for their lack of understanding by using large design margins for condensers, by specifying off-gas compressors for zero calculated gas rates, and by greatly oversizing off-gas compressors. These practices can still result in lack of capacity for installations such as in this case study. Even very rough estimates of local equilibrium effects can be far better than conventional calculations for series condensation.

For a single shell and moderate deviations from universal VLE, a reasonable sub-cooling delta temperature can sometimes be used for simulation and design. In extreme cases, calculations for zones in each shell may be necessary to give good simulation or design. For this case study, the zone method would probably have been required if the condenser paths had been many times longer than in a double split-flow configuration.

CASE STUDY 1.14 SIMULATOR HYDRAULIC PREDICTIONS: TO TRUST OR NOT TO TRUST?

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In this case study, a simulator hydraulic calculation led a plant to expect a capacity gain almost twice as high as the tower revamp actually achieved.

History A refinery vacuum tower was debottlenecked for a 30% capacity gain by replacing 2-in. Pall rings in the wash and heavy vacuum gas oil (HVGO) sections with 3-in. modern proprietary random packings. Only about 15–20% capacity gain was achieved. It was theorized that above this throughput vapor maldistribution set in

and caused the tower to lose separation. The refinery sought improvements to vapor distribution in an effort to gain the missing 10–15%.

Troubleshooting A vacuum manometer pressure survey showed that at the point where the tower lost separation the pressure drop was 0.65 in. H₂O/ft packing. Based on air/water measurements, many suppliers' packages take the capacity limit (or flood point) to occur at a pressure drop of 1.5–2 in. H₂O/ft packing. Work by Strigle (473), Rukovená and Koshy (418), and Kister and Gill (257, 259) demonstrated that such numbers are grossly optimistic for modern, high-capacity random and structured packings. Using published flood data, Kister and Gill (257, 259) showed that, for random and structured packings, the flood pressure drop is given by

$$\Delta P_{\text{flood}} = 0.115 F_P^{0.7} \quad (1)$$

where ΔP_{flood} is the flood pressure drop (in. H₂O/ft packing) and F_P is the packing factor (ft⁻¹). This equation was shown to give a good fit to experimental data (many of which were generated by suppliers) and was later endorsed by Strigle (473) with a slight change of coefficient. For the high-capacity packing in the vacuum tower, the packing factor was 12. Equation 1 predicts that ΔP_{flood} was 0.65 in. H₂O/ft packing, which coincided with the limit observed by the refinery.

For hydraulic calculations, gas velocity usually is expressed as a *C*-factor (C_S), (ft/s), given by

$$C_S = U_S \left(\frac{\rho_G}{\rho_L - \rho_G} \right)^{0.5} \quad (2)$$

where U_S is the gas superficial velocity based on tower cross-sectional area (ft/s), ρ is the density (lb/ft³), and the subscripts G and L denote gas and liquid, respectively. The *C*-factor essentially is a density-corrected superficial velocity. The fundamental relevance of the *C*-factor is discussed elsewhere (251).

Based on a flood pressure drop of 0.65 in. H₂O/ft packing derived from Equation 1, the maximum efficient capacity of the new 3-in. random packing calculated by the Kister and Gill method (251) was at a *C*-factor of 0.38 ft/s. This is about 17% higher than the maximum efficient capacity for the previous 2-in. Pall rings, just as the refinery observed.

According to the supplier's published hand correlation, which we believe was similar to the one in the computer simulation, the maximum efficient capacity of the packing was at a *C*-factor of 0.43 ft/s, which is 13% higher than observed. This high *C*-factor matched a pressure drop of between 1 and 1.5 in. H₂O/ft packing, well above the value where the packing reached a capacity limit.

Epilogue Based on the hydraulic calculation in the computer simulation, the refinery expected that changing the 2-in. Pall rings to the 3-in. high-capacity random packing would increase capacity by 30%. In real life, just over half of the capacity increase materialized. The half that did not materialize is attributed to the optimistic prediction from the simulation.

CASE STUDY 1.15 PACKING HYDRAULIC PREDICTIONS: TO TRUST OR NOT TO TRUST

Background This case presents a number of experiences which were very similar to Case Study 1.14. In each one of these, vendor and simulator predictions for a packed tower were optimistic. In each one of these, the Kister and Gill equation (257, 259) gave excellent prediction for the maximum capacity. The Kister and Gill equation is

$$\Delta P_{\text{flood}} = 0.115 F_P^{0.7} \quad (1)$$

where ΔP_{flood} is the flood pressure drop (in. $\text{H}_2\text{O}/\text{ft}$ packing) and F_P is the packing factor (ft^{-1}).

Tower A This was a chemical tower, equipped with wire-mesh structured packing with a packing factor of 21. The tower ran completely smoothly until reaching a pressure drop of 1 in. $\text{H}_2\text{O}/\text{ft}$ packing, then would rapidly lose efficiency. This compares to a flood pressure drop of 0.97 in. $\text{H}_2\text{O}/\text{ft}$ packing from Equation 1. Simulation prediction (both vendor and general options) predicted a much higher capacity.

Tower B This was a chemical tower equipped with random packing with a packing factor of 18. This column would rapidly lose efficiency when the pressure drop increased above 0.67 in. $\text{H}_2\text{O}/\text{ft}$ packing. This compares to a flood pressure drop of 0.87 from Equation 1. The measurement was slightly lower than the prediction because the vapor load varied through the packings, so much of the bed operated at lower pressure drop. Simulation prediction (both vendor and general options) predicted a much higher capacity. Similar to Case Study 1.14, the plant initially theorized that the shortfall in capacity was due to vapor maldistribution.

Tower C This was a chemical absorber equipped with random packing with a packing factor of 18. The highest pressure drop at which operation was stable was 0.8 in. $\text{H}_2\text{O}/\text{ft}$ packing. Above this, the pressure drop would rapidly rise. This compares to a flood pressure drop of 0.87 from Equation 1. Simulation predictions (both vendor and general options) were of a 20% higher capacity.

Tower D Random packing installed in a chemical tower fell short of achieving design capacity. The vendor method predicted flooding at a pressure drop of 1.5 in. $\text{H}_2\text{O}/\text{ft}$ packing. With a packing factor of 18, Equation 1 predicted that the packing would flood much earlier at a pressure drop of 0.8 in. $\text{H}_2\text{O}/\text{ft}$ packing. The packing flooded at exactly that pressure drop.

CASE STUDY 1.16 DO GOOD CORRELATIONS MAKE THE SIMULATION HYDRAULIC CALCULATIONS RELIABLE?

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What follows is an actual letter circulated by an engineer working for a reputable company. The names of the correlations cited, as well as a few sentences, were changed to protect those involved.

We have had a problem recently with the prediction of flooding in packed towers using the Smith correlation for packed tower capacity in the Evertrue Simulator. We used this for sizing a packed tower at 400 psia. The program predicted a percentage flood of 56 percent using the Smith correlation. The vendor predicted 106 percent of flood, and 123 percent of the packing useful capacity.

The Evertrue calculation is based on an article by Smith in Quality Chemical Engineering magazine. Smith's method, in turn, depends on an earlier correlation by Jones, also published in an article in Quality Chemical Engineering.

These correlations are neither well developed nor tested. Neither of these articles (Smith's and Jones') have undergone very close scrutiny, nor are the correlations from well-known textbooks or journals that have a tradition of peer review. One of the failings is the use of the correlation at high pressure with hydrocarbon systems. Smith's correction factor for high pressures produces numbers that are unreasonably high. There is no indication that this factor is supported either by correlation or by theory. In addition to the lack of credibility of Smith's values, the correlation of Jones, used as the basis of the Smith method, appears inaccurate for the high-pressure systems.

For these reasons, I would not recommend use of the Evertrue Smith correlation, regardless of the system pressure, for predicting whether or not a packed tower will work. Instead, the 1960 correlation included on Evertrue should be used. This correlation is based on well-known methods, and can be found in "Perry's Handbook." It predicts the tower would be at 96 percent of flood, compared to the 106 percent predicted by the vendor, which is much closer than the Smith correlation.

In either case, calculations must be verified by the packing vendor. I recommend that the vendor verifies the results even for estimates.

What Really Happened In our experience, both the Smith and the Jones correlations are excellent. The correlation that leaves a lot to be desired for modern packing calculations is the 1960 one. Nevertheless, the letter's author appeared to have reached the converse conclusion.

It is a sad fact of life that correlation authors always examine their correlations for good statistical fit but seldom properly explore and clearly define their correlation limitations. On page 39 of Ref. 259, Kister and Gill remark: "An excellent fit to experimental data is insufficient to render a packing pressure-drop correlation suitable for design. In addition, the correlation's limitations must be fully explored."

In contrast to the letter writer's comment, the problem is more acute in articles that are peer reviewed. These contain correlations based on fundamental models that are inherently complex. This complexity makes it very difficult to properly identify the limitations. A peer review offers little help unless the reviewer spends several days checking the calculations. This rarely happens.

The Smith correlation works very well for vacuum and atmospheric pressures, perhaps up to 50 psia. It was never intended to apply to 400 psia. Unfortunately, Smith's article only contained a hint of the pressure limitation but no firm statements to that effect. It, therefore, went into the Evertrue simulator without a warning flag

above 50 psia. In this case, the 1960 correlation was found to work well. This appears to be a case of two wrongs making a right.

Epilogue There are many correlations in the published and proprietary literature for which the limitations are neither well explored nor well defined. Limitations unflagged in the original articles remain unflagged in the simulator version.

Despite the letter writer's wrong conclusion, his bottom line is broadly valid. A simulator correlation cannot be trusted, even when the correlation is good, unless the correlation's limitations are known and included in the simulation. An independent verification, say, by a supplier or an independent method, is a good idea. When *Distillation Design* (251) was compiled, special effort was made to talk to authors of good correlations, with the objective of exploring their limitations and filling in the missing blanks. For instance, the pressure ranges for the application of Smith's correlation were listed in *Distillation Design* almost two years before the above letter was written.

Chapter 2

Where Fractionation Goes Wrong

Fractionation issues featured very low on the distillation malfunctions list for the last half century (255). Only two issues rated a mention, intermediate-component accumulation and two liquid phases. Neither of these made it to the top 20 distillation malfunctions. This contrasts the author's experience. Intermediate-component accumulation is experienced frequently enough to justify a place in the top 20, maybe even close to the 10th spot. The large number of cases of intermediate-component accumulation reported in this book will testify to that. In many cases, the accumulation led to periodic flooding in the tower. Other problems induced by the accumulation include corrosion, product losses, product contamination, and inability to draw a product stream.

A second liquid phase, either present where undesirable or absent where desired, was troublesome in several case histories, most from chemical towers. In many cases, issues in the overhead decanter or its piping induced an undesirable phase either into the reflux or into the product. Presence or absence of a second liquid phase caused not only separation issues and production bottlenecks but in some cases also violent reactions, damage, and explosions.

Other fractionation issues include insufficient reflux, insufficient stages, insufficient stripping, and excessive bottom temperatures. Although basic to fractionation, it is amazing how often it is overlooked. Unique multicomponent issues include absorption effects in wide-boiling mixtures and location of side draws. Azeotropic and extractive distillation have their own unique challenges.

CASE STUDY 2.1 NO REFLUX, NO SEPARATION

Contributed by Ron F. Olsson, Celanese Corp.

The feed to a 55-tray tower came in 10 trays below the top. The tower was separating an alcohol as the distillate from a glycol as a bottom product. A simulation detected that the losses of glycol in the distillate were excessive. The glycol losses were

estimated to cost about \$250,000 per year. Further investigation revealed that the reflux had been eliminated. Apparently, the reflux rate was cut out during the 1970s, when energy savings were most important. Over the years, this mode of operation became the norm. Further, corrosion of the trays reduced their efficiency, causing the separation to deteriorate.

The glycol losses were drastically cut once the reflux was reintroduced.

CASE STUDY 2.2 HEAVIER FEEDSTOCK IMPEDES STRIPPING

Contributed by Dmitry Kiselev and Oleg Karpilovskiy, Koch-Glitsch, Moscow, Russia

Installation A diesel hydrotreating unit was revamped to a dewaxing process. Due to increase in production of wild naphtha and gases, the diesel stabilizer was revamped also. The revamp design proposed to use a fired heater reboiler to provide the desired diesel flash point. The refinery did not have enough time to revamp the heater, so the unit started with stripping steam injection under the bottom tray, instead of the heater reboiler circuit.

Problem After several months of operation, the refinery decided to complete the unit revamp. The heater reboiling circuit was made operational while the steam line was disconnected. The result was surprising: The flash point of diesel decreased by 20°C, even though design specifications of the reboiling circuit (flow rate and heater outlet temperature) were achieved.

Investigation The first suspicion was that tray damage occurred during start-up, but checking of this required a shutdown or gamma scans, which were expensive options in that location. A complete set of process data was collected instead and a tower simulation prepared. The feed composition was surprisingly much heavier than design. The ASTM D86 50% percent point increased from 265 to 320°C. The reflux rate was half the design value. The simulation showed almost no vapor in the stripping part of the column. The heater outlet temperature could not be increased beyond 330°C to generate additional vapor due to vibration of the 75-m-long heater outlet line. The simulation showed that heater outlet temperatures even as high as 350–360°C would have been insufficient for achieving the diesel flash point specification.

The reason for poor operation was the new feed composition. The reason for the heavier feedstock was a revamp of the atmospheric tower of the crude oil distillation unit that took place at the same time as the last stage of the revamp of the hydrotreating unit. The crude tower revamp added a diesel draw in order to send light diesel directly to product blending and to dewax the heavy diesel only.

Solution During the next turnaround, the stripping steam line was reconnected. Simultaneous use of stripping steam and reboiling allowed the tower to achieve the product specification.

CASE STUDY 2.3 POOR H₂S REMOVAL FROM NAPHTHA HYDROTREATER STRIPPER

Contributed by Mark Pilling, Sulzer Chemtech, Tulsa, Oklahoma

Installation Naphtha hydrotreater stripper, stripping H₂S from naphtha.

Problem Tower had been operating fine for extended period. At a later time, it could no longer meet H₂S specification for bottom product.

Troubleshooting The tower was operated at the same bottom temperature as it always had been, but the reflux rate was much lower than normal. Investigations revealed that the feed to the unit had become considerably heavier. For this heavier feed, the operating bottom temperature was too low to provide sufficient stripping for H₂S removal.

Solution Bottom operating temperature and reflux ratio were raised to ensure proper H₂S removal.

Morals Tower operation needs to vary to accommodate changing feedstocks. Operators need to be trained to recognize the critical operating set points.

CASE STUDY 2.4 HEAVIES ACCUMULATION INTERRUPTS BOIL-UP

Contributed by Ron F. Olsson, Celanese Corp.

Figure 2.1 shows a system that recovered product from residues. The system removed product continuously as an overhead product from column C1. The heavy residues were periodically removed from drum D1.

Occasionally, the temperature of drum D1 would rise to the point where the reboiler could no longer boil it. The plant would then dump the drum content out of the bottom (route B). When the drum contents were dumped, lots of lights were lost in the dump. When the reboil ceased, liquid from column C1 dumped and much of it ended in the D1 drum dump.

The problem was fixed by removing bottom residue streams continuously from both points A and B. It took some trial and error to correctly set the bottom rate.

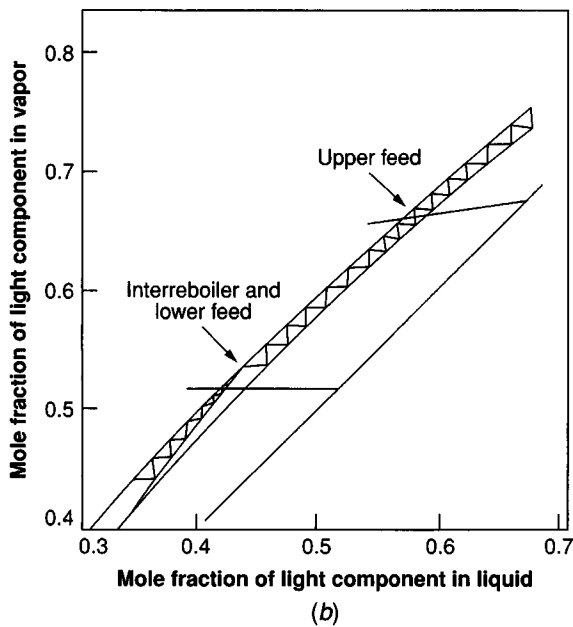
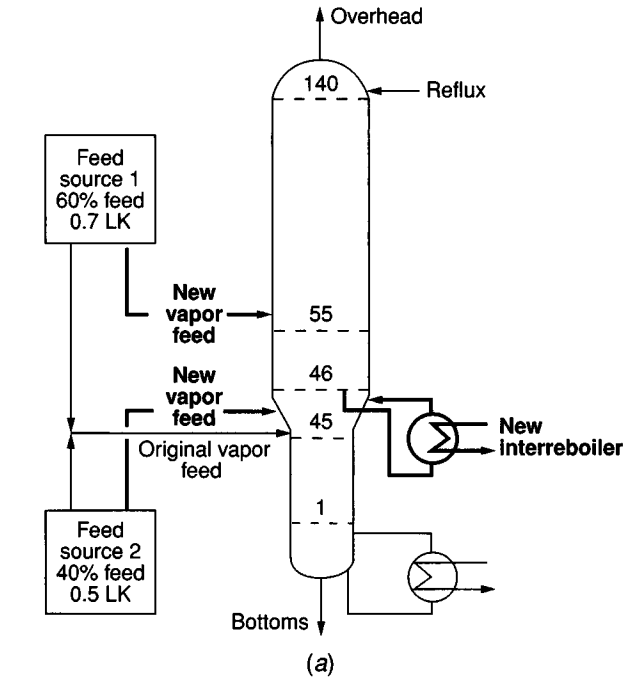


Figure 2.2 Proposed C₂ splitter debottleneck: (a) proposed changes, adding an interboiler and splitting the feeds; (b) McCabe-Thiele diagram that clearly warned of imminent pinch. (From Ref. 254, 276. Reproduced with permission. Copyright © (1995) AIChE. All rights reserved.)

Hydraulic calculations showed that the rectifying section would be barely capable of handling the increased throughput. The stripping section was undersized for the higher throughput and would require an expensive retrain with specialty high-capacity trays.

Alternative Scheme A clever alternative scheme was conceived with a potential of slashing the revamp costs as well as saving energy. There was scope to have the feed enter as two separate streams. One contained 70% ethylene, made up 60% of the feed, and was to enter on tray 55 (Fig. 2.2a). The second contained 50% ethylene, made up 40% of the feed, and was to enter on tray 45. To unload the bottom section, an interboiler was to be added at tray 46, supplying about 10% of the total column heat duty. Since the interboiler was to convert 10% of the liquid into vapor, the vapor and liquid traffic in the narrow-diameter section below would diminish by 10%. This unloading was enough to accommodate the post-debottleneck throughput.

In principle, the interboiler was to unload the narrow-diameter section that bottlenecked the tower. Splitting the feed was to assist in expanding the stripping section from 45 to 55 trays without adversely affecting separation in the rectifying section. The extra stripping trays were needed to accommodate for the lower V/B (stripping ratio) generated below the interboiler.

A computer simulation showed that the scheme would work well. There were no convergence problems, nor was there anything about the simulation that may indicate a potential problem. The scheme received the go-ahead.

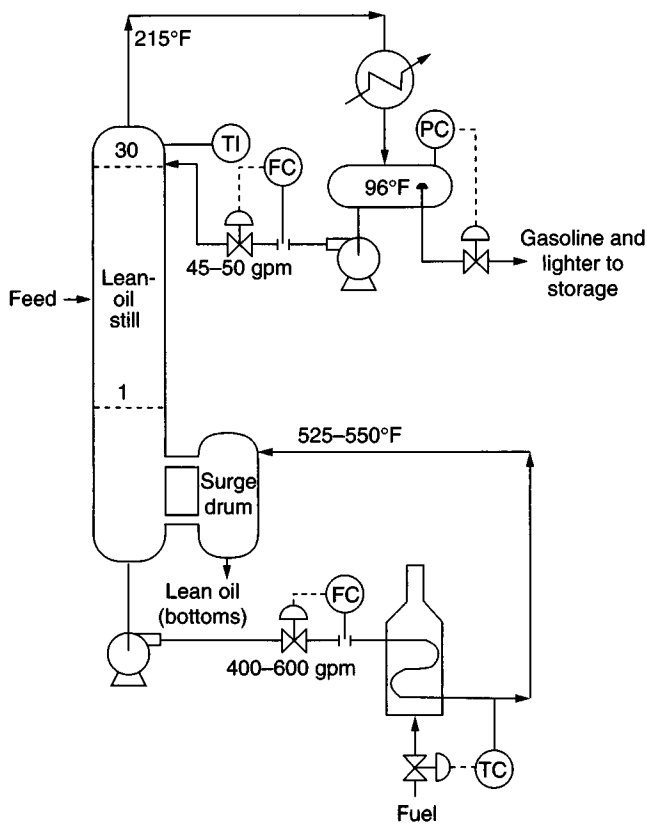
Just prior to going into the final design, a McCabe–Thiele diagram was constructed to explore hidden traps (Fig. 2.2b). The pinch just below the interboiler was glaring.

Postmortem The interboiler caused the V/B for the section below to diminish almost to the minimum stripping. Although hydraulically the interboiler would have fulfilled its function, the column may not have achieved the design separation due to the pinch. Alternatively, to overcome the pinch, the operator would have needed to raise both the reflux and reboil and would have possibly encountered a hydraulic bottleneck.

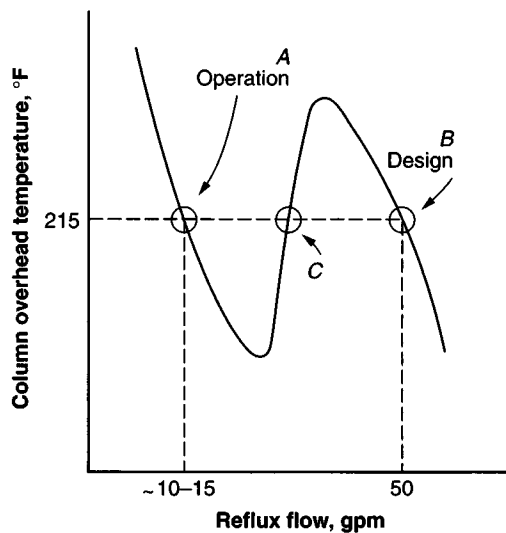
CASE STUDY 2.6 TEMPERATURE MULTIPLICITY IN MULTICOMPONENT DISTILLATION

Henry Z. Kister and Tom C. Hower, reference 263. Reproduced with permission. Copyright © (1987) AIChE. All rights reserved

Installation A lean-oil still in an absorption–refrigeration gas plant (Fig. 2.3a). This still was the last step of purification of the absorption oil before the oil was returned to the plant absorber to absorb heavy components from natural gas. Feed to the still was the absorption oil, containing the absorbed gasolines and some LPG. Lighter components were removed from the oil upstream of the still. Lean oil left



(a)



(b)

Figure 2.3 Multicomponent still that showed temperature multiplicity: (a) lean-oil still; (b) variation of lean-oil still top temperature with reflux. (From Ref. 263. Reproduced with permission. Copyright © (1987) AIChE. All rights reserved.)

as the still bottom product, while gasoline and LPG were the top product. The still operated at 210 psig. Note the large temperature difference between the bottom and top of the still.

The main objective of the still was to keep gasoline out of the column bottom. This was achieved by the furnace outlet temperature control. The reflux rate was trimmed by manually adjusting the flow controller set point, so as to give a reasonably constant column overhead temperature. The reflux drum was flooded, and liquid level in the condenser was used to control column pressure.

Problem The plant absorber appeared to be malfunctioning. It did not absorb all the heavy ends out of the gas.

Investigation The initial boiling point (IBP) of the lean oil leaving the still was low, which indicated the presence of a substantial quantity of gasoline in the still bottom. This suggested that the still was malfunctioning. The still showed no signs of flooding. The control temperature, the overhead temperature, and the reflux rate appeared to be at their design values. The composition of the top product was not analyzed.

Solution The problem was caused by insufficient reflux rate. The low reflux rate was unnoticed because of an incorrectly sized orifice plate in the still reflux line. When the orifice plate was replaced and the correct reflux flow set, the plant observed a large permanent increase in fuel usage and a large drop in the apparent quantity of absorption oil, indicating that the gasoline was being stripped off the bottom. Following this, the plant absorber started functioning normally and absorbing heavy ends out of the gas.

Analysis The problem was particularly difficult to detect because of the unusual behavior of the overhead and bottom temperatures. Normally, when a substantial amount of light impurity is present in the bottom, one would expect the bottom temperature to drop; when a substantial amount of heavy impurity is present in the column overhead, one would expect this temperature to rise. Over-reboiling can bring the bottom temperature back up, but in such a case, one would expect the top temperature to rise further above design.

The above considerations are generally valid for binary distillation and often, but not always, for multicomponent separations. This case is an example of a multicomponent distillation where the above considerations do not apply.

In general terms, at the low reflux rates the column was operated as a gasoline–LPG separator instead of an absorption oil–gasoline/LPG separator. This lowered temperatures throughout. However, the column was over-reboiled; this returned the bottom and top temperatures to their design values. This is explained in detail below.

At the low reflux ratio, a substantial fraction of the gasoline reached the bottom. This would have caused a lower temperature at the base of the column, but the control system increased the reboil rate (i.e., over-reboiled) to keep the bottom temperature up at design. Because of the low reflux ratio, however, the over-reboil action boiled over a significant fraction of absorption oil and perhaps most of the gasoline. The

column probably fractionated out most, but not all, of the absorption oil. The mixture arriving at the top tray therefore contained the LPGs, some gasoline, and a small quantity of absorption oil. The presence of the absorption oil acted to increase the top tray temperature; the absence of gasoline that was lost to the bottom acted to decrease it. By varying the reflux rate as in normal operation, one could keep the top temperature at its design value.

Variations of the column overhead temperature are shown in Figure 2.3*b*. Under all these conditions, bottom temperature was controlled at 525–550°F. The column overhead initially operated at point *A* at the low reflux conditions. At the correct reflux rate, the overhead temperature operated at point *B*. Note the existence of point *C* on this curve, at which an increase in reflux rate causes an increase in overhead temperature. This operating condition (point *C*) has actually been observed in this type of column.

CASE STUDY 2.7 COMPOSITION PROFILES ARE KEY TO MULTICOMPONENT DISTILLATION

Contributed by Frank Wetherill (retired), C. F. Braun, Inc.,
Alhambra, California

Installation A product column in a specialty chemical plant producing a heavy, water-soluble glycol product. The process is similar to that described in Case Study 15.1. The column separated glycol product from high-boiling residues. The column is shown in Figure 2.4*a*.

Problem Although water was removed from the column feed and water-forming reactions were suppressed by lowering the base temperature in a manner similar to that described in Case Study 15.1, a very small quantity of water (about 0.1%) was still present in the product. It was economical to remove even that amount of water from the product.

Investigation This amount of water was very small and could have originated either in the column feed or from water-forming condensation reactions at the column base. Tackling this problem at the source would have been difficult.

It was realized that the product was very hygroscopic. Therefore, it was suspected that after the product was condensed and subcooled in the overhead condenser it reabsorbed water from the inerts stream.

Solution It appeared beneficial to withdraw the product upstream of the point where it was being subcooled. A suitable point was the top tray of the column. The column was modified to withdraw product from this tray, as shown in Figure 2.4*b*. This eliminated the water problem.

Postmortem The relative volatility for glycol–water separation was large (the atmospheric boiling point of the glycol was greater than 400°F). Any liquid water present in the reflux stream therefore easily vaporized on the top tray.

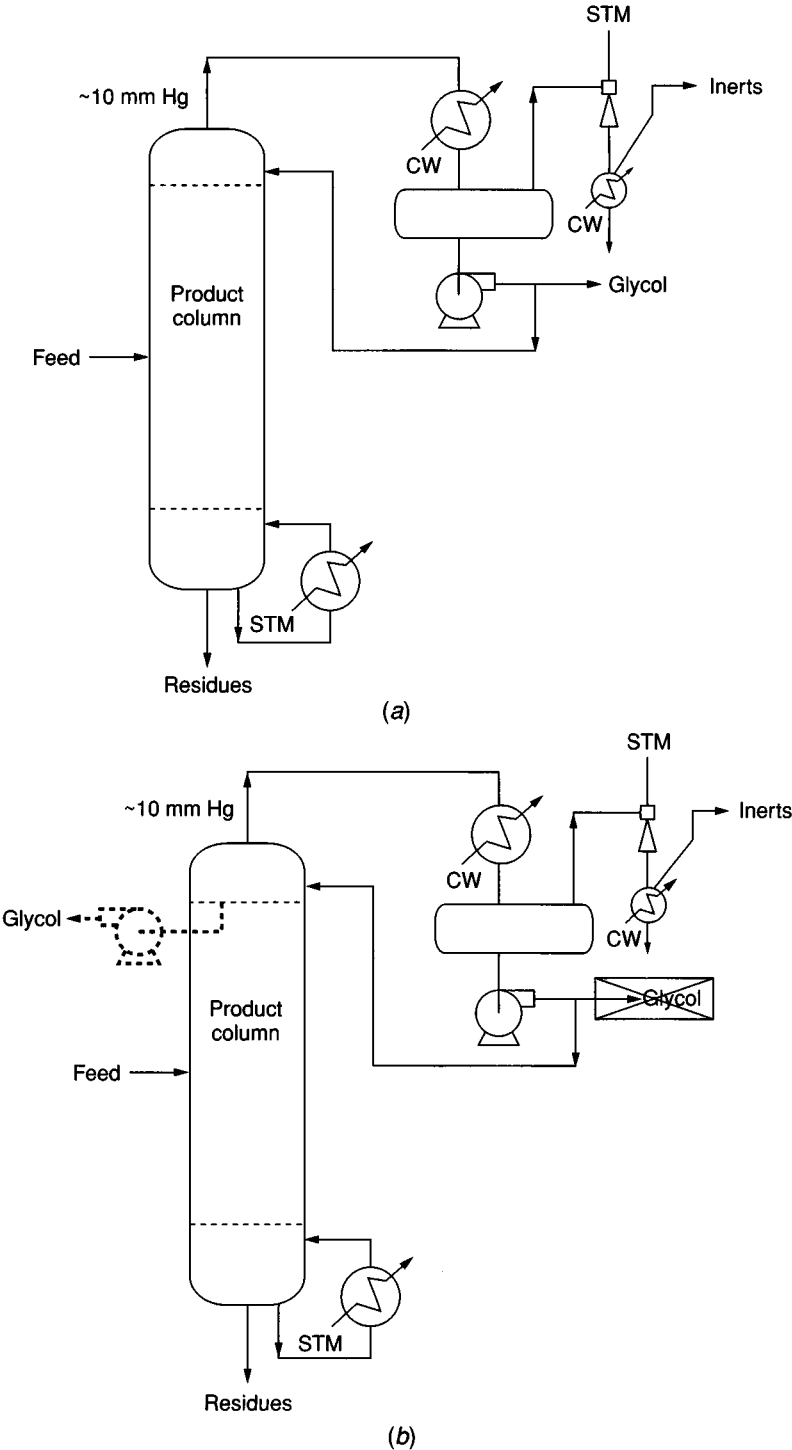


Figure 2.4 Glycol product column: (a) initial; (b) modified.

It may appear that withdrawing water from the top tray, instead of from the reflux drum, would have enriched the product with the heavier impurity because the condenser stage was no longer available for the product–residue separation. This enrichment, however, was minimal, because even before the modification the condenser behaved as a total condenser from the product–residue separation viewpoint (product was withdrawn as liquid) and had therefore contributed little to the product–residue separation.

Another Plant A glycol/residue tower in a completely different plant and operated by a different company experienced a somewhat similar problem. In that case, the amount of water was small. Instead of escaping in the inerts route, the water was condensed and refluxed back into the tower. Over a period of time, water built up in the overhead loop and adversely affected product purity. The problem was solved by periodically running the reflux drum liquid to a flash tank.

CASE STUDY 2.8 COMPOSITION PROFILE PLOT TROUBLESHOOTS MULTICOMPONENT SEPARATION

Henry Z. Kister, Rusty Rhoad, and Kimberly A. Hoyt, references 254, 273.
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Engineers seldom bother plotting composition profiles in multicomponent distillation. Like the McCabe–Thiele and Hengstebeck diagrams, column composition profiles (generated from the compositions calculated by the simulation; Refs. 243 and 251 have detailed examples) are a superb analytical and troubleshooting tool that provides visualization that simulations do not. Undetected abnormalities often reveal themselves as a column malfunction after start-up. This case shows how a composition profile identified a very unforgiving column design.

Background A chemical vacuum tower containing structured packing (Fig. 24.1a and 2.5) separated a heavy key (HK) component from an intermediate key (IK) component in its lower section. There was a specification of 0.3% maximum IK in the bottom and 1.0% maximum HK in the vapor side product. Feed to the column contained many other components that were lighter or heavier than the keys.

Problem While the bottom product was on specification, the vapor side product contained about 10% HK, which was several times higher than the design.

Troubleshooting Initial suspicion was a malfunction of the structured packing or the distributors. The design height equivalent of a theoretical plate (HETP) was on the low side, but not grossly so. The lower bed was simulated by eight stages; six or seven would have been a closer estimate. The distributor design was found to be good, and the distributor was successfully water tested and debugged at the manufacturer's shop before being installed in the tower. The VLE data were examined. While not perfect, the volatility estimate was quite reasonable.

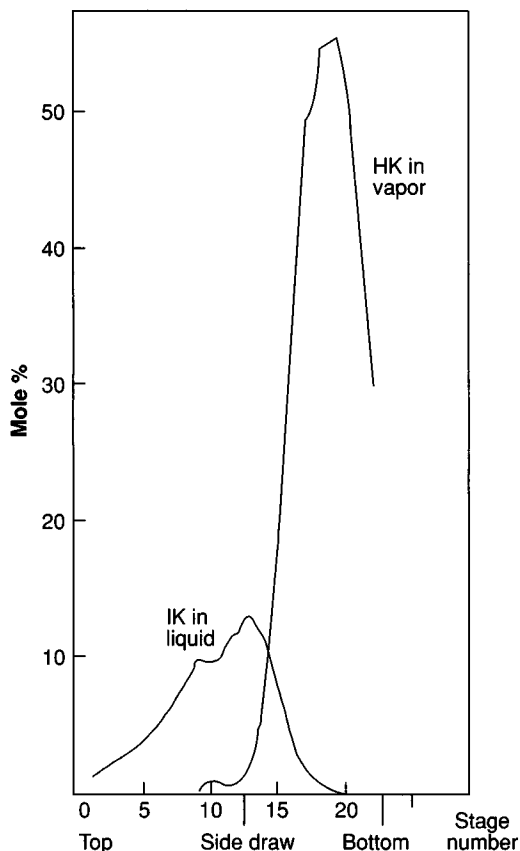


Figure 2.5 Composition profile pinpoints sensitivity of heavy key. (From Ref. 254, 273. Reproduced with permission. Copyright © (1996) AIChE. All rights reserved.)

Next, plugging of the packing or distributors was suspected. Extensive field tests, described in detail in Case Study 4.9, were performed and showed that the tower operated well below flood and that both the pressure drop and flood point were well inline with predictions. Gamma scans verified that distribution below the flood point was quite reasonable and there were no signs of plugging.

Likely Cause During the troubleshooting, the design simulation was revisited and the composition profiles plotted. The profiles plot the concentrations of each component in the liquid (one plot) and the vapor (a second plot) against the theoretical stage number. Figure 2.5 is a condensed version, singling out the IK in the liquid and the HK in the vapor. These were the prime actors in the current problem. The diagram shows an extremely steep peak for the HK in the vapor. Stage 18 vapor contains 55% HK. By the time the vapor draw-off is reached on stage 13 (five stages up), the HK concentration is supposed to drop to 1%. On stage 14, the HK concentration is about 7%, and on stage 15, it is 18%. Figure 2.5 therefore depicts a very unforgiving composition profile.

Achieving the design separation depends upon the lower packed bed successfully developing eight theoretical stages. Should this number fall a stage or two short, the concentration of HK in the vapor side draw would skyrocket, with product going severely off specification. Sources that can make the number of stages fall short of expectation by one or two were (and usually are) abundant. These include a slightly optimistic design HETP, inaccuracies in VLE, differences between design and actual feed compositions, relatively small scale fouling or maldistribution, and even disturbances to the feed and the heating and cooling media.

CASE STUDY 2.9 WATER ACCUMULATION CAUSES CORROSION IN CHLORINATED HYDROCARBON TOWER

Installation A tower separating HCl and HC gases from chlorinated HCs (Fig. 2.6). There was a very small amount of water (~ 3 ppm) in the feed.

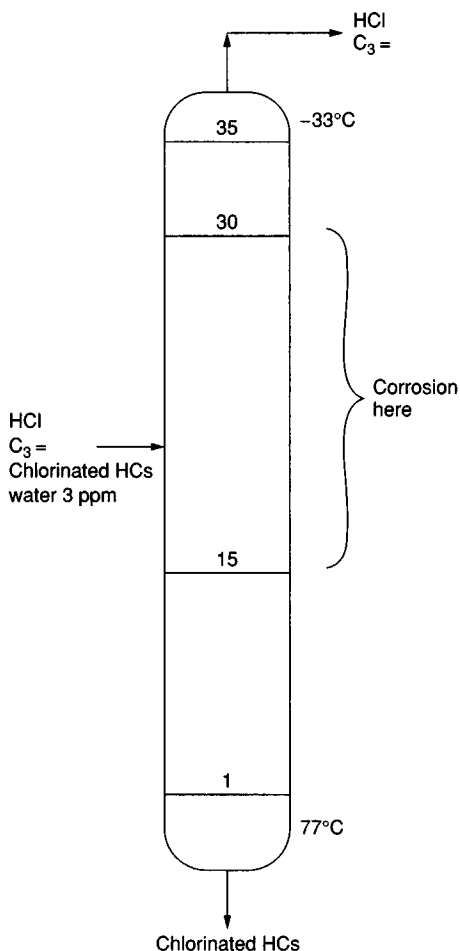


Figure 2.6 Water accumulation in chlorinated hydrocarbon column.

Problem There was severe corrosion on trays 15–30. There was no corrosion at the top 5 trays and the bottom 15 trays. The column run length was less than a month; afterward it needed shutting down to replace the trays.

Cause Top temperature was too cold, and bottom temperature too hot, to allow water to escape. In the bottom section, repulsion of water by the chlorinated HCs increased its volatility. As a result, the water became trapped in the tower and concentrated near the feed. The accumulation could be predicted using a NRTL or UNIQUAC model, but not using ideal solution or equation-of-state models.

Solution The problem was resolved by replacing trays 15–30 by trays fabricated from Hastelloy C.

Related Experience A decomposition reaction took place near the bottom of one chemical tower, yielding a corrosive compound. The boiling point of that compound was well below the tower overhead temperature. It therefore accumulated and corroded trays in the middle of the tower.

CASE STUDY 2.10 HICCUPS IN A REBOILED DEETHANIZER ABSORBER

Installation A refinery reboiled deethanizer absorber (Fig. 2.7). The top section of the tower used a naphtha stream to absorb C_3 and C_4 HCs from a gas stream that went to fuel gas.

Feed to the tower contained a small amount of water. Free water was removed in the feed drum upstream of the tower, but the separation was not perfect. In addition, the small quantity of water dissolved in the HC feed would not be removed in the feed drum.

Bottoms from the tower went to a debutanizer that operated much hotter than the deethanizer. The debutanizer recovered the C_3 and C_4 HCs in the top product, leaving gasoline as the bottom product.

Problem Plant economics favored maximizing recovery of C_3 and C_4 in the deethanizer bottoms. To achieve this, the control temperature in the stripping section was lowered. The system worked well for 2–3 days following the change. Then the debutanizer pressure suddenly shot up, and a large slug of water was observed to fill the boot of the debutanizer reflux drum. A few minutes later the water disappeared. Two to three days later the process repeated. The possibility of steam or water leaks was investigated, but none were found.

Solution The tower was returned to its previous mode of operation with the higher deethanizer control temperature.